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FEASIBILITY OF A REGENERATIVE HIGH TEMPERATURE AMINE ABSORPTION PROCESS FOR THE CONTROL OF SULFUR DIOXIDE EMISSIONS FROM STACK GASES

Heinz P. Beutner, et al

Little (Arthur D.), Inc.
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U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
NATIONAL CENTER FOR AIR POLLUTION CONTROL

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FEASIBILITY OF A REGENERATIVE HIGH TEMPERATURE AMINE ABSORPTION PROCESS FOR THE CONTROL OF SULFUR DIOXIDE EMISSIONS FROM STACK GASES

by

Heinz P. Beutner
Walter R. Niessen
Henry E. Haley
William S. Emerson

for the

U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE

NATIONAL CENTER FOR AIR POLLUTION CONTROL

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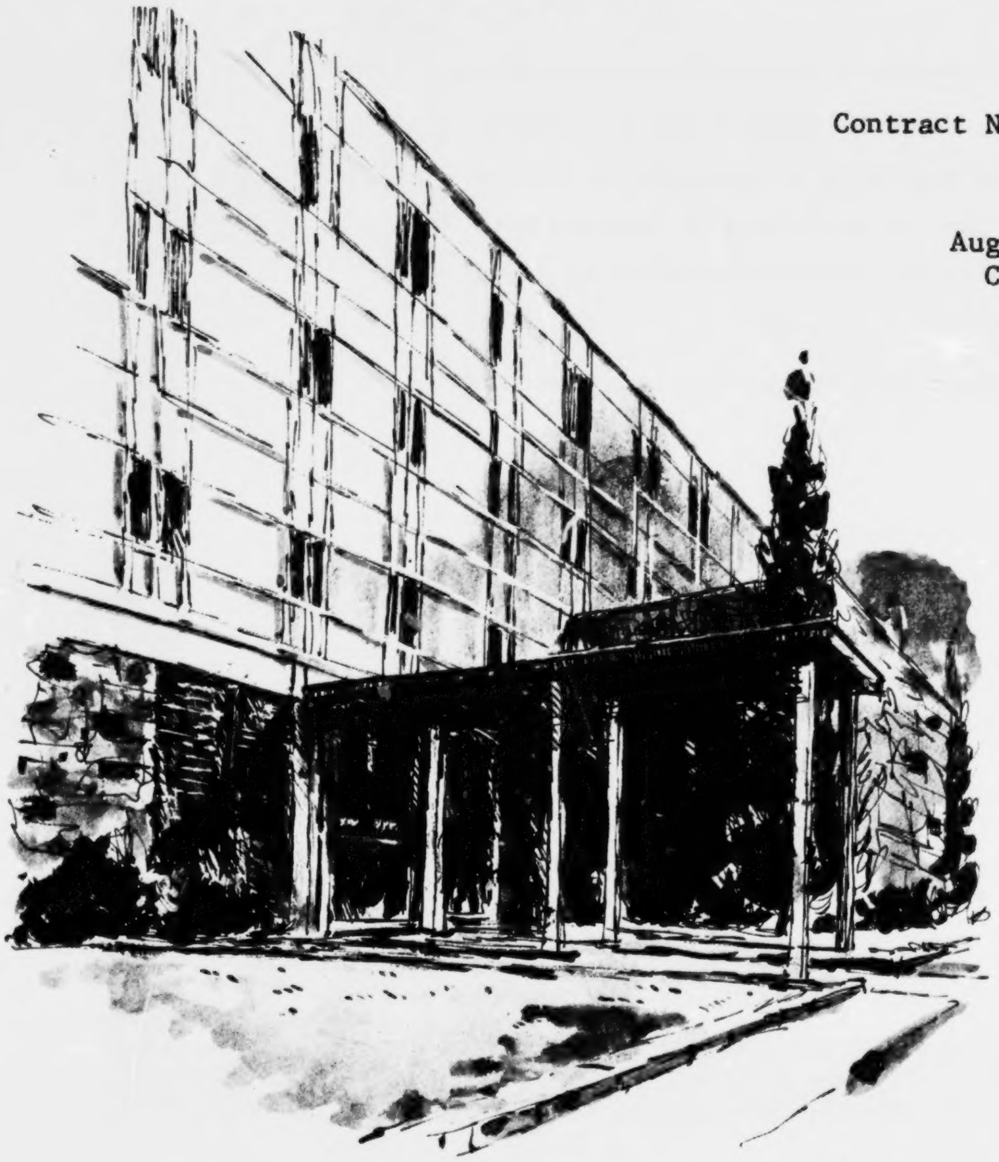

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Contract No. Ph 86-68-57

Errata

Page 24, Figure 5: read

2 TEA:1 SO_2 for 2 SO_2:1 TEA

Page 40: read

$4\ SO_3^{2-} \rightarrow S^{2-} + 3\ SO_4^{2-}$

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SUMMARY

A. PURPOSE AND SCOPE

This study was undertaken to evaluate the feasibility of a high temperature regenerative amine absorption process (HiTRAAP) for the removal of sulfur dioxide from stack gases. The objective of the projected process was (a) to eliminate the need for cooling the stack gases to the temperature range of an aqueous base scrubbing solution and to avoid subsequent reheating of the exit gas to give it buoyancy and (b) to eliminate the water plume, which may result from an aqueous scrubbing process.

The scope of this program consisted principally of an extension of sulfur dioxide solubility data for aqueous amine solutions to temperatures above 100°C. Based on such data a suitable temperature range was to be selected for a sulfur dioxide absorption-desorption cycle. A number of amines selected on the basis of high thermal and oxidation stability and low volatility were to be evaluated and preliminary engineering cost estimates were to be obtained for the selected processes. The program also included an investigation of irreversible reactions of the amine with sulfur dioxide, sulfur trioxide or nitrogen oxides in the flue gas.

In the course of the program the major emphasis had to be shifted to this last aspect of the process. As a consequence of the observed chemistry the scope of the program was extended further to include exploratory evaluation and engineering cost analyses of a number of chemical recovery processes.

B. CONCLUSIONS

1. Certain amines have very high solubilities for sulfur dioxide at flue gas temperatures and at flue gas sulfur dioxide concentrations in the presence of moisture. We found at 100°C, 1% sulfur dioxide and 10% moisture the following absorption capacities (in grams of sulfur dioxide per 100 grams of the amine):

• triethanolamine	23
• tetraethylenepentamine	70
• pentahydroxyethyl diethylenetriamine	27
• hexahydroxyethyl triethylenetetramine	18

These capacities correspond roughly to the composition of neutral amine-salts (mole ratio of sulfur dioxide to amine-nitrogen = 1:2)

2. The sulfur dioxide is removed from the equilibrium with the gas phase by a disproportionation reaction, which produces primarily dithionate, $S_2O_6^{2-}$, as well as tri- and pentathionate ($S_3O_6^{2-}$ and $S_5O_6^{2-}$). The sulfur dioxide absorption capacities therefore should be little dependent on the sulfur dioxide concentration in the gas or on the temperature within the temperature range of this reaction. The scrubbing efficiency should increase with higher temperatures as the rate of the disproportionation reaction increases. Because of this irreversible disproportionation of sulfur dioxide, the original process concept of sulfur dioxide absorption in amines at flue gas temperatures and desorption at higher temperatures (HiTRAAP) is not feasible.

3. Irreversible reactions between the absorbed sulfur species and the amine occur at more elevated temperatures characteristic for each amine. Triethanolamine reacts at 130°C to form organic sulfur compounds and polymeric products. Tetraethylenepentamine is stable in the presence of the sulfur species to 170°C. At this temperature the amine reduces all species to hydrogen sulfide, which is liberated as gas; the amine is oxidized to an amide.

4. The recovery of the sulfur values from the amine requires chemical methods rather than straight pyrolysis. Some methods indicated are:

- Resin or liquid ion exchange
- Precipitation of the sulfur anions as insoluble salts

- Reduction, oxidation or disproportionation to sulfur compounds which can be easily isolated.

Potential routes for desorption are recommended for future work on the basis of preliminary engineering cost projections for several alternative process schemes.

5. We carried out a comparative engineering cost analysis of eight potential high temperature amine flue gas scrubbing processes employing postulated chemical regenerations. Although based on simplifying assumptions, the data for an 800 megawatt power plant indicate that several processes might be attractive economically:

- Reduction of the sulfur species to elemental sulfur, either directly with hydrogen sulfide as reducing agent, or via reduction to hydrogen sulfide by hydrogen or reducing gas and Claus reforming (operating credit of 0.17 mills/kwh for direct reduction).
- Liquid ion exchange extraction of the sulfur species, for example, with a water-insoluble, long chain amines or quarternary amine hydroxides and sulfur recovery as ammonium sulfate (operating credit 0.07 mills/kwh).
- Resin ion exchange and recovery as ammonium sulfate (operating cost 0.04 mills/kwh).
- Precipitation of the sulfur species with lime, assuming a credit for the resultant salt equivalent to the value of the contained sulfur (operating cost 0.08 mills/kwh).

6. Overall, we conclude that a process based on sulfur dioxide absorption from flue gases in amines in the temperature range of the flue gas (200 to 350°F) is conceptually feasible if the regeneration of the amine and the recovery of sulfur values are carried out chemically rather than by thermal stripping. A suitable amine for this process is tetraethylenepentamine.

The practical feasibility of the process has not been established as yet. This study has not evaluated the loss of amine due to irreversible side reactions caused by nitrogen oxides, sulfur trioxide and oxygen in the flue gas and has not given consideration to the loss of amine and the possible contamination problem due to the vapor pressure of the amine. Finally the regeneration of the amine by any of the chemical routes has not been evaluated experimentally.

C. RECOMMENDATIONS

On the basis of the experimental findings during this program on the high temperature regenerative amine absorption process (HiTRAAP) and the engineering cost analyses of potential chemical amine regeneration routes, we recommend a follow-on program with the following scope:

1. Investigation of the feasibility of chemical methods of regeneration of the amine and recovery of the sulfur values
2. Evaluation of second generation amines for the projected process.
3. Evaluation of the effect of irreversible reactions between the preferred amine and sulfur trioxide and nitrogen oxides in the flue gas.
4. Bench scale cycling tests with simulated high temperature flue gas.
5. Refined engineering cost estimates.

I. INTRODUCTION

This program originally was designed to establish the feasibility of HiTRAAP (High Temperature Regenerative Amine Absorption Process) by measuring physical and engineering parameters of the projected process and carry out a preliminary engineering cost analysis. In the course of the study, especially during attempts to desorb sulfur dioxide thermally and regenerate the amine, we realized, however, that sulfur dioxide undergoes an irreversible disproportionation reaction which prevents its recovery by thermal means. Therefore, the major part of this project This report is ~~subsequently was~~ directed toward elucidating the irreversible reactions in the amine-sulfur dioxide system and explor~~ing~~s potential methods of chemically recovering the sulfur values. ~~We believe that~~ this effort is ~~was~~ successful insofar as insight is ~~was~~ gained into the reactions of sulfur dioxide in amines at elevated temperatures and a better perspective of the required recovery processes is ~~was~~ achieved. Furthermore, in order to gain a perspective of the economics of the modified amine process, engineering cost estimates are ~~were~~ carried out for potential process schemes involving chemical recovery. The program changes were within the objective of this project to evaluate the feasibility of a regenerative high temperature amine scrubbing process for the control of sulfur dioxide emission from stack gases.

# A significant result of this research work was the observation of the disproportionation of the absorbed sulfur dioxide in the amine into di- and polythionates, for example, according to the following overall equation $20\ SO_2 + 8\ H_2O \xrightarrow{\text{yields}} 6\ S_2O_6^{2-} + S_3O_6^{2-} + S_5O_6^{2-} + 16\ H^+$. ~~We believe that~~ this reaction might have ramifications extending to a variety of sulfur dioxide sorption processes in the temperature range of stack gases (200 to 350°F). This report, therefore, includes both a discussion of the evidence for this reaction occurring in the amine system and a brief review of some known chemistry of the sulfur species produced.

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II. SULFUR DIOXIDE ABSORPTION CAPACITIES OF SELECTED AMINES AT ELEVATED TEMPERATURES

1. Screening of Pre-Selected Amines

The first phase of this program consisted of an evaluation of the sulfur dioxide absorption capacities at elevated temperatures of a number of selected amines. Candidate amines had been specified in our proposal on the basis of high boiling points and expected resistance to oxidation and thermal degradation at high temperatures in the presence of flue gas. We deleted two compounds from the originally proposed list: triethylenetetramine, which proved to be too volatile; and triaminobenzene, which could not be prepared from its salts because of the instability of the free amine. Instead, we included three new compounds: tetraethylenepentamine and two ethoxylated amines, which were prepared in our laboratory from diethylenetriamine and triethylenetetramine respectively. The latter two compounds are closely related to triethanolamine and were included in the evaluation because of the high sulfur dioxide absorption shown by the latter.

The apparatus for determining sulfur dioxide solubilities in amines at elevated temperatures is shown in Figure 1. Nitrogen gas containing 1% sulfur dioxide was purchased from the Matheson Company. The gas was passed through a fritted glass sparger into samples of 50-100 gms of the amine held in a constant temperature bath until the exit gas showed a sulfur dioxide concentration equal to that in the entering gas. The concentrations in the two gases were compared by means of a gas chromatograph (Perkin Elmer, Ucon Column; the column shows variations in the sulfur dioxide peak height and, therefore, is not suitable for absolute measurements. At concentrations below 0.1% sulfur dioxide it is difficult to obtain any reproducible response). The gas flow rate was about 1 liter per minute, but varied over a wide range when back pressure built up in the system because of a rise in the viscosity of the amine. The rate is equivalent to roughly 1.6 gms sulfur dioxide per hour. Solubilities were determined both in the presence and absence of water vapor in the gas phase. The test gas was humidified at 50°C to give a water vapor concentration of about 12.2%. The results of the sulfur dioxide solubility

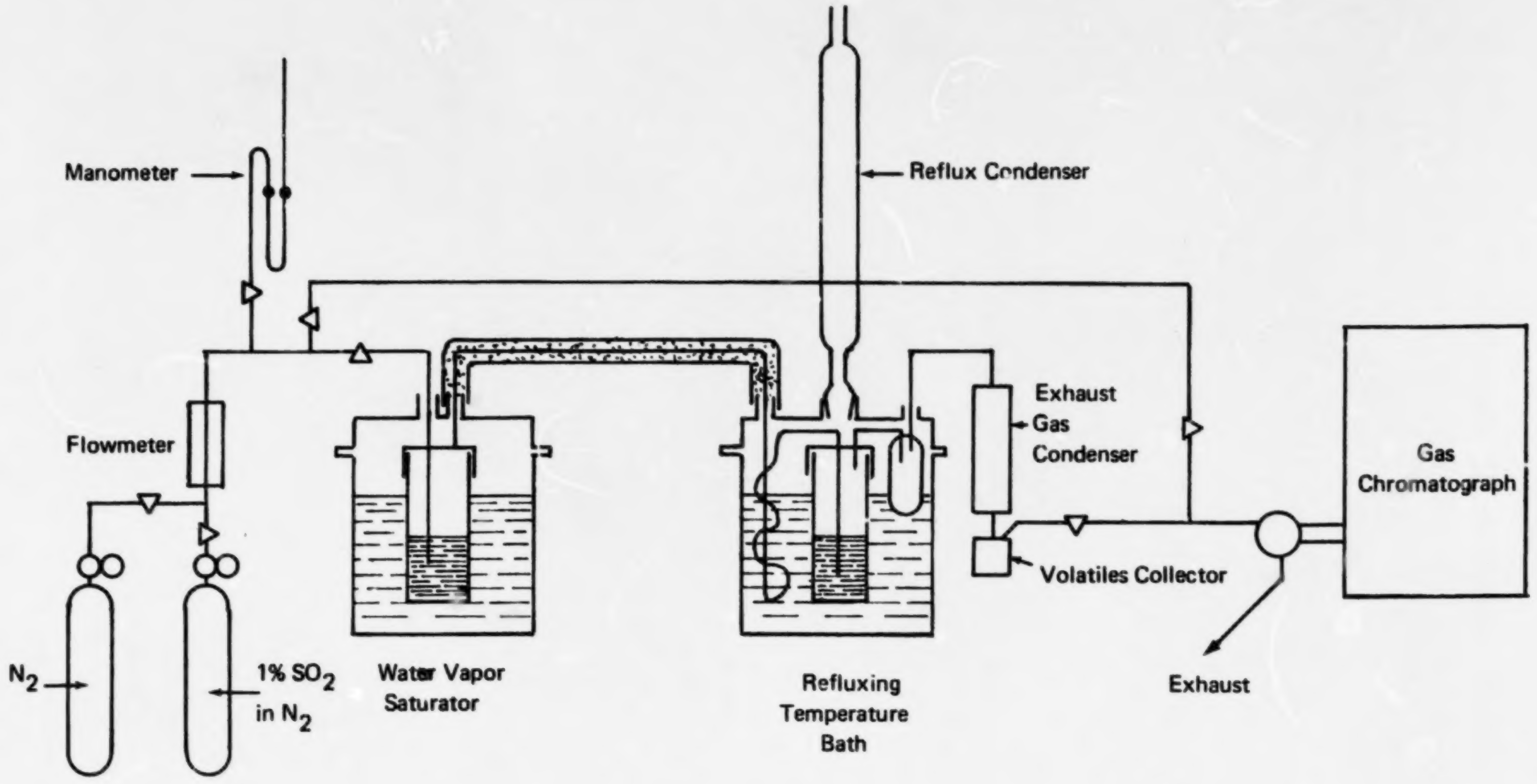
Manometer
Reflux Condenser
Flowmeter
Exhaust Gas Condenser
Gas Chromatograph
Volatiles Collector
N_2
1% SO_2 in N_2
Water Vapor Saturator
Refluxing Temperature Bath
Exhaust

FIGURE 1 EXPERIMENTAL APPARATUS FOR DETERMINING SULFUR DIOXIDE SOLUBILITY AT ELEVATED TEMPERATURES

determinations at 100 and 150°C are given in Table 1. The time required to reach equilibrium saturation was recorded as a rough measure for the amount of sulfur dioxide absorbed by the sample. The samples were analyzed for sulfur and nitrogen.[1] We determined the content of amine in each sample on the basis of the nitrogen analysis, and computed the absorbed sulfur dioxide in gms per 100 gms of amine. The difference to 100% of amine plus sulfur dioxide (referred to in this text as "difference analysis") is a rough measure of the presence of other constituents in the sample, primarily water. However, some of the starting materials were not pure compounds and had nitrogen contents which deviated from the theoretically expected values. Nitrogen data obtained for some of the starting materials are summarized in Table 2, and were used to compute the content of the impurities (assumed to be nitrogen free) in these amines. Also shown are the results of water determination by the Karl Fischer method (except for tetraethylenepentamine which caused problems in the attempted analysis) and these data indicate that none of the amine starting materials contained significant amounts of water. We must, therefore, assume that the amines which show significant deviations from theory by nitrogen analysis contained compounds of either higher or lower nitrogen content.

The results in Table 1 indicate very little absorption of sulfur dioxide in dipyridylpropane (VI), diaminodiphenylmethane (IV), and tricaprylamine (I) both in the presence and absence of water vapor in the test gas. Extremely large capacities are shown by the four other amines. These are discussed as follows.

In the tests with tetraethylenepentamine (VII) equilibrium conditions were not attained and the exit gas was in all cases free of sulfur dioxide according to our gas chromatographic analysis. The runs were terminated because the viscosity of the amine at 100°C became excessively high. The amine absorbed 70.0 gms of sulfur dioxide per 100 g of amine under test conditions in the presence of 12% water in the gas. The products were highly viscous liquids which were moderately discolored in tests in the

---

[1] All analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Table 1

Sulfur Dioxide Solubilities in Selected Amines at Elevated Temperatures. (Test gas containing 1% SO_2, bal. N_2)

Amine Number	Amine (Molecular Weight)	Max. Capacity (g SO_2 per 100g Amine)(1)	Run No.	Humidity of Test Gas(2)	Temp. (°C)	Time to Equilib.(4) (Hrs.)	Analysis(6) SO_2 (%)	Analysis(6) N (%)	Calculated Data Amine (%)	Calculated Data Per 100g Amine SO_2	Calculated Data Per 100g Amine Other(7)	Remarks
VI	1,3-(4,4"-dipyridyl) propane MW = 198	N = 32.35 A = 64.7	5	dry	100	4	0.34	13.6	96.1	0.4	3.5	greenish solid
			7	wet	100	2	0.28	13.7	96.9	0.3	2.8	pink solid
			17	(3)	100	2	0.76	11.3	79.5	0.8	19.7	red solution
IV	4,4'-diaminodiphenyl methane MW = 200	N = 32.0 A = 64.0	3	dry	100	5	0.38	13.3	95.0	0.4	4.6	cryst. in brown oil
			6	wet	100	3	0.09	13.6	96.2	0.1	3.7	crystalline
I	Tricaprylamine MW = 353	N = 9.1 A = 18.2	2	dry	100	2	1.28	3.05	76.9	1.7	21.0	yellow liquid
VII	Tetraethylene-pentamine MW = 186	N = 86.0 A =172.0	8	dry	100	35(5)	31.7	22.3	59.2	53.5	14.5	dark, viscous liquid
			9	wet	100	59(5)	36.9	19.8	52.6	70.0	19.9	brown, viscous liquid
			15	wet	100	12(5)	10.4	24.6	65.3	15.9	37.0	yellow, viscous liquid
III	Triethanolamine MW = 149	N = 21.45 A = 42.9	4	dry	100	37	28.1	6.9	73.4	39.0	-2.2	brown, viscous liquid
			11	wet	100	19	17.9	7.3	77.8	23.1	6.2	colorless, viscous;2.5% water
			16	wet	100	12(5)	17.6	6.9	73.4	23.9	12.1	colorless, viscous liquid
			18	wet	150	17(5)	12.2	10.0	106.3	11.5	-17.3	black tar
			21	wet	150	25	33.2	10.5	112.2	29.6	-40.2	black tar
VIII	Pentahydroxyethyl diethylenetriamine MW = 323	N = 29.75 A = 59.5	13	dry	100	15	22.2	12.4	95.3	23.3	-18.5	black, very viscous liquid
			14	wet	100	17	23.1	11.1	85.3	27.1	-9.6	light brown, viscous
			19	wet	150	5(5)	4.0	15.0	115.0	3.5	-16.9	black tar
IX	Hexahydroxyethyl triethylenetetramine MW = 410	N = 21.5 A = 43.0	10	dry	100	21	19.9	11.6	84.9	23.4	-5.6	dark brown, very viscous
			12	wet	100	10	15.8	11.7	85.6	18.5	-1.3	yellow, viscous; 1.4% water
			20	wet	150	35(5)	15.6	13.2	96.8	16.1	-13.0	black tar

(1) N = neutral salt (amine: SO_2 = 2:1); A = acid salt (amine: SO_2 = 1:1)

(2) The wet gas contains about 12.2% water vapor

(3) 75% aqueous solution of amine

(4) At a gas flow rate of approximately 1L/min and between 50-100g amine

(5) Equilibrium not reached in this run

(6) Analysis by Schwarzkopf Microanalytical Laboratory

(7) Difference to 100% (amine + SO_2)

Table 2

SOME PROPERTIES OF SELECTED AMINES

Amine Number	Amine	M.P. (°C)	B.P. (°C)	B.P. (°C)(1)		Water(2) (%)	Nitrogen (%)		Impurity	
				10% Water	25% Water		Theory	Found	(%)	Per 100g Amine
VI	1,3-(4,4"-dipyridyl) propane	62	211/5mm	120	114	0.6				
IV	4,4' -diaminodiphenyl methane	93	250/15mm	not miscible		0.4				
I	Tricaprylamine	--	367	not miscible		0.1				
VII	Tetraethylene pentamine	--	151/1mm	n.a.		n.a.	37.6	31.6	16.0	19.1
III	Triethanolamine	--	360	136	113	0.4	9.4	9.2	1.8	1.8
VIII	Pentahydroxyethyl diethylenetriamine	--	n.a.	145	114	0.5	13.0	14.5	-11.4	-10.2
IX	Hexahydroxyethyl triethylenetetramine	--	n.a.	131 (13% water)		0.4	13.7	12.2	10.0	11.1

---

(1) Determined experimentally

(2) Determined by Karl Fisher titration

presence of water, and nearly black in a test in the absence of water vapor. The "difference analysis" showed large weight gains under all of the test conditions, but the analysis of the starting material (Table 2) indicated a deficiency in nitrogen corresponding to nearly 19 gms of a nitrogen-free impurity per 100 gms of the amine. Thus the "difference analysis" data indicated a slight component loss under dry conditions, no change under wet conditions at 100°C and a large loss at 150°C.

Triethanolamine (III) absorbed about 90% of the quantity of sulfur dioxide theoretically expected for an acid salt (mole ratio amine: SO_2=1:1) under the conditions of a dry, 1% sulfur dioxide test gas at 100°C. Equilibrium was reached slightly above the composition for a neutral salt (22.0 gms of sulfur dioxide per 100 gms of amine) in the presence of water in the test gas. The sulfur dioxide absorption product of triethanolamine was colorless for wet test gas, and light brown for dry gas. The product obtained in the presence of water vapor contained about 2.5% free water according to Karl Fischer titrations. According to the "difference analysis", samples obtained from a wet test gas at 100°C contained between 6 and 12% water which may be partially chemically bonded. A sample prepared from a dry test gas showed a weight loss of about 2gms per 100 gms of amine according to the "difference analysis". Very large weight losses were shown by samples tested at 150°C with wet test gas. These samples were black tars and obviously were degradation products of a reaction between sulfur dioxide and triethanolamine. The high nitrogen analysis for these products suggests that parts of the molecule were split off and volatilized, leaving a residue high in nitrogen. Similar products were obtained during attempts to regenerate the triethanolamine thermally; further examinations of the high temperature reaction product are reported later. (Section III)

The two ethoxylated amines (VIII and IX) were similar in behavior in the presence of water vapor at 100°C. Equilibrium saturation appeared to be reached for both amines at compositions corresponding to slightly less sulfur dioxide than required for the neutral salt. Very little color change was observed. The darker color of the products obtained under dry conditions at 100°C appeared to be indicative of some reaction between sulfur dioxide and the amine. As in the case of triethanolamine, considerable reaction appeared to occur between sulfur dioxide and the ethoxylated amines at 150°C under wet conditions. The "difference analysis" indicated weight losses for both amines under all test conditions. However, the analysis of the pure starting materials (Table 2) was equivalent to a deficiency of about 10 gms per 100 gms of pentahydroxyethyl diethylenetriamine and an excess of about 11 gms per 100 gms of hexahydroxyethyl triethylenetetramine. Thus the "difference analysis" data in Table 1 indicate roughly no or little change under wet conditions at 100°C, but considerable losses under dry conditions at 100°C and wet conditions at 150°C.

2. Some Conclusions Concerning the Sulfur Dioxide Absorption in Amines and the Effects of Water

The screening tests (Table 1) identified a number of amines which have high absorption capacities for sulfur dioxide at 100°C and above, both in the presence and absence of water vapor. We have no acceptable explanation at this time why no absorption occurred in the first three amines of Table 1. We might suspect that the two aromatic amines, as well as tricaprylamine, are weaker bases than the other four amines. Also, the ability to hydrate and the high polar character of the last four amines might be a contributing factor.

The nature of the absorption product of sulfur dioxide in amine has been subject to discussion. Normal salt formation is feasible in the presence of water in the amine but in the absence of water a sulfur dioxide adduct should form. There is some evidence for this view. Taking triethanolamine as example, the absorption of sulfur dioxide at 100°C under dry conditions proceeded to a mole ratio of nearly one amine to one sulfur dioxide, with very few other changes in composition as indicated by the "difference analysis". This is agreeable with the formulation of the product as $(HOCH_2 \cdot CH_2)_3N \cdot SO_2$. Under wet conditions the sulfur dioxide absorption proceeded to a mole ratio slightly in excess of one sulfur dioxide to two amines and the "difference analysis" indicated a weight gain of 6-12 gms per 100 gms of amine, which is in the right order of magnitude for the required uptake of 12 gms of water per 100 gms of amine to form the neutral triethanolammonium salt, $[(HOCH_2CH_2)_3NH]_2SO_3$. Consequently the sulfur dioxide absorption under dry conditions could be viewed as a Lewis acid-base reaction and the absorption under wet conditions as a Bronsted acid-base reaction. The thermal stability of the Lewis adduct of amine and sulfur dioxide to 100°C and above appears unusual, though.

As shown later in this report, we obtained evidence for a different type of reaction occurring in the amine. It involves a disproportionation of sulfite (or sulfur dioxide or pyrosulfite) into sulfur anions of higher and lower oxidation states. The principal reaction can be represented by the following equation:

$$\underset{\text{sulfite}}{4\ SO_3^{2-} + 4H^+} \xrightleftharpoons{-H_2O} \underset{\text{pyrosulfite}}{2S_2O_5^{2-}} \longrightarrow \underset{\text{dithionite}}{S_2O_4^{2-}} + \underset{\text{dithionate}}{S_2O_6^{2-}}$$

The dithionite can undergo further disproportionation and polymerization reactions, leading among others to tri- and pentathionate. An overall reaction such as:

$$20\ SO_2 + 8H_2O \longrightarrow S_5O_6^{2-} + S_3O_6^{2-} + 6S_2O_6^{2-} + 16H^+$$

requires 0.4 mole of water per mole of sulfur dioxide compared to 1.0 mole to form sulfite or bisulfite and 0.5 moles to form pyrosulfite. The absorption of one mole of sulfur dioxide in one mole of triethanolamine from a dry test gas would therefore require the presence of approximately 2.5 gms of water in 100 gms of the amine.[2] That much water in the commercial product appears feasible. We found 1.8% in triethanolamine by "difference analysis" and 0.4% by the Karl Fischer method, which does not measure strongly bonded water (Table 2).

---

[2] If we assume formation of even higher polymerized thionates (e.g. up to $S_{12}O_6^{2-}$) the required amount of water can decrease, for example to 0.17 moles per mole of sulfur dioxide or 1.0 gms per 100 gms of amine under the conditions described.

Furthermore, there is evidence for some oxidation and dehydration of the amine under dry conditions; in triethanolamine and ethoxylated amines the reaction appears to abstract water from the ethanolic hydroxyl group to give an olefinic bond, followed by further oxidation to a carbonyl. Infrared spectra of amines reacted under dry conditions (compare Table 1) always showed absorptions characteristic for olefinic unsaturation and for carbonyl groups; also the products were always slightly discolored. The oxidation and discoloration was not observed in the presence of water (compare also Table 5 in Section III).

We may thus conclude that the disproportionation at elevated temperatures of sulfur dioxide in di- and polythionates can take place under all conditions unless water producing reactions are rigorously excluded. Water may be considered a disproportionation catalyst which is consumed in the reaction.[3]

The apparent solubility of sulfur dioxide in amines at elevated temperatures appears to be due to an irreversible reaction (disproportionation) and the apparent saturation is reached, when the system has become neutral (pH 7). The apparent solubility therefore should be independent of the partial pressure of sulfur dioxide in the gas phase and of the temperature as long as the temperature is above a certain critical range. High temperatures might increase the scrubbing efficiency of the system by increasing the rate of the disproportionation reaction.

There is some evidence (compare desorption by steam, Section IV) that sulfur dioxide added to the system at 100°C beyond the neutral point, is absorbed in a reversible reaction and this solubility consequently is dependent on the partial pressure and the temperature. However, this reversible solubility appears to be negligible at low sulfur dioxide partial pressures and 100°C and therefore insufficient for a flue gas absorption process.

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[3] The catalytic effect of water on reactions of sulfur dioxide is well established. The Karl Fischer method for the determination of water relies on the reaction of sulfur dioxide with iodine in pyridine/methanol and the reaction proceeds only until all water is consumed.

3. Investigation of the Absorption of Sulfur Dioxide in Triethanolamine

Based on the results of the screening tests, commercial availability and low price, triethanolamine was considered the prime candidate material throughout the remainder of the study. As shown later, this was to some extent an unfortunate choice, because this amine reacts with sulfur species at the relatively low temperature of about 130°C. Tetraethylenepentamine is more stable and would have been a better model system for the study of sulfur dioxide absorption and desorption.

The changes in composition and acidity with increasing saturation of triethanolamine with sulfur dioxide at 100°C were measured as shown in Table 3. The acidity was measured both by NMR and pH in dilute aqueous solutions. The sulfur dioxide concentration in the amine and the acidity data are plotted in Figure 2 as a function of time of exposure to the sulfur dioxide containing test gas. The data show that equilibrium saturation was reached at a composition of slightly above a neutral amine sulfite salt (mole ratio $TEA:SO_2 = 2:1$) and that the pH of a 1% aqueous solution at this composition is about 7 (neutral). We also estimated the water content of the amine by means of the "difference analysis" described earlier. In spite of wide variations due to the large error in this estimation, we can observe that the water absorption from the gas phase appears to parallel the sulfur dioxide absorption and approach the theoretically required level of 6 gms per 100 gms of the amine at the composition of the neutral salt $2\ TEA \cdot H_2O \cdot SO_2$.

NMR spectra of the triethanolamine-sulfur dioxide absorption product were taken primarily for the purpose of identifying possible reaction products from the interaction of sulfur dioxide and/or water with triethanolamine at the elevated temperature. None of the NMR spectra taken during this program showed signals which might be consistent with any major chemical change in the triethanolamine molecule. Even NMR spectra of discolored or tar-like products obtained under dry conditions at 100°C or wet conditions at 150°C showed only the signals consistent with triethanolamine under varying acidity. It is believed that the high temperature reactions between triethanolamine and sulfur dioxide

Table 3

SULFUR DIOXIDE ABSORPTION IN TRIETHANOLAMINE AT 100°C FROM GAS CONTAINING 1% SO_2, 10% H_2O, Bal. NITROGEN

Time (hrs)	Composition (g per 100 g amine)		Saturation (% of theory)(2)	NMR - Spectrum (Acidity)			pH (1% Solution)
	SO_2	H_2O(1)		δ_A (ppm)	δ_B (ppm)	$\Delta\delta$ (Hz)	
			Exp. A-III-22A				
0	0	1.8	0	3.68	2.74	57	10.0
1	3.2	2.4	7.5	3.71	2.72	54	
3	7.3	2.2	17.0	3.77	2.84	48	8.4
5	11.5	4.9	26.8	3.88	3.20	40	7.8
7	17.4	7.0	40.5	3.93	3.36	34	7.35
9	21.3	3.4	49.7	3.97	3.41	33	6.9
			Exp. A-III-16				
12	23.9	12.1	55.7	3.95	3.36	34	
			Exp. A-III-11				
19	23.1	6.2	53.9	3.94	3.34	35	7.1

---

(1) Water is based on difference to 100% of amine (N-analysis) plus sulfur dioxide (S-analysis).

(2) Theory assumes a mole ratio SO_2:TEA = 1:1 (42.9g SO_2 per 100 g TEA).

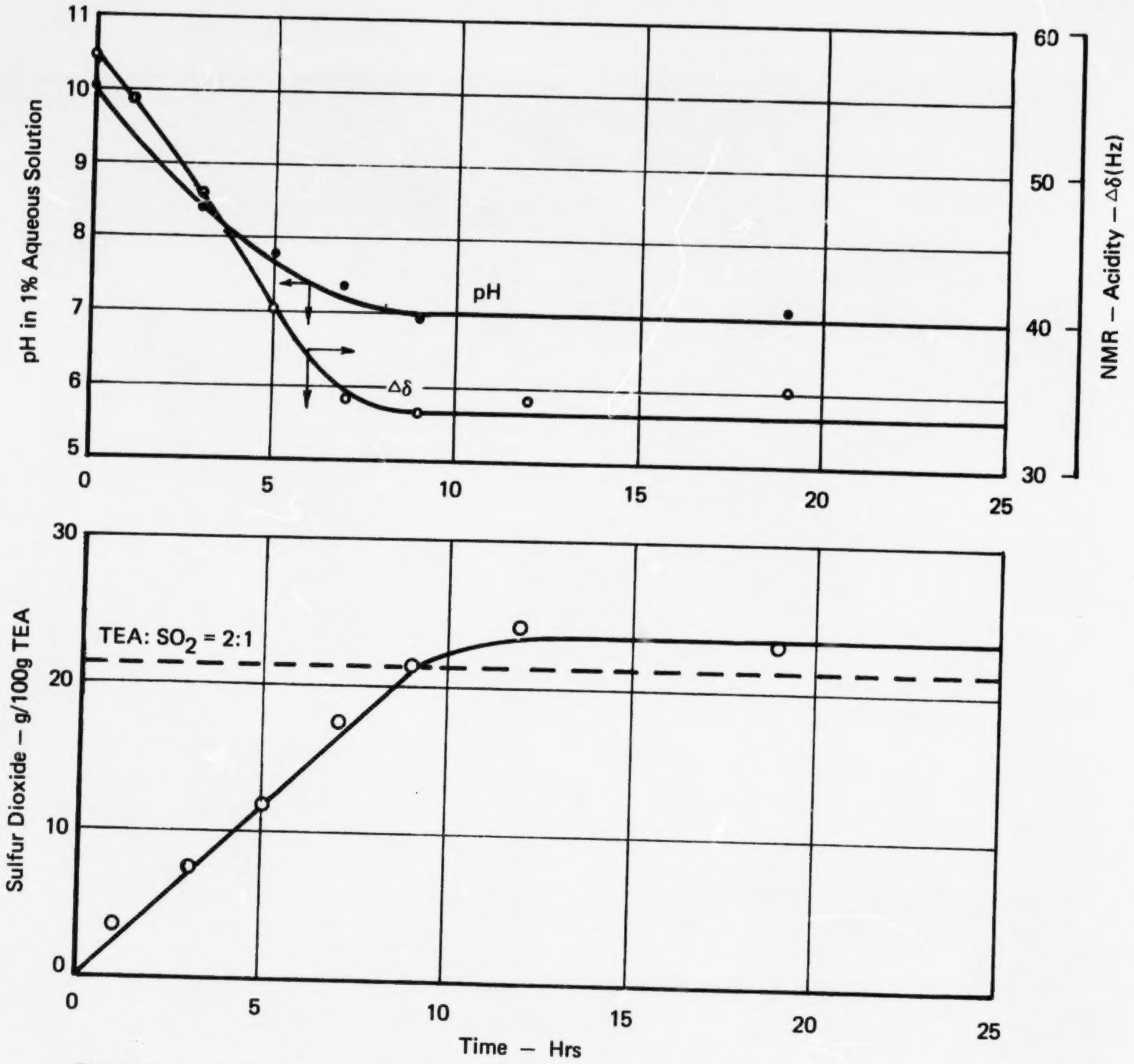

FIGURE 2 SULFUR DIOXIDE ABSORPTION IN TRIETHANOLAMINE AT 100°C FROM A TEST GAS CONTAINING 1% SO_2, 10% H_2O, BALANCE N_2

or its disproportionation products produced predominantly non-polar and/or polymeric, water insoluble products which did not appear in the NMR spectrum of the aqueous solution. The minor formation of carbonyl groups and unsaturation in samples at 100°C in the absence of moisture as indicated by IR spectra, did not affect the NMR signals. The NMR spectra are sensitive indicators of acidity.[4]

The spectra were run in about 10% aqueous solutions. Absorption due to triethanolamine was observed at 3.68δ and 2.74δ relative to tetramethylsilane (internal standard). The absorptions consisted of two sets of triplets corresponding to the methylene groups adjacent to the hydroxyl group and the tertiary amino-nitrogen, respectively. The phenomenon of spin-spin interaction between hydrogens on adjacent carbon atoms was responsible for splitting each resonance into triplets. The absorption of sulfur dioxide in the amine resulted in an acidity change which affected the resonance position of the methylenes adjacent to the hydroxyl group to a lesser extent than that of those adjacent to the tertiary nitrogen. One can, therefore, take the distance ($\Delta\delta$) between the two signals as an arbitrary measure of the acidity of the amine environment. As indicated in Table 3, the maximum shifts observed for the two signals in a sample saturated with sulfur dioxide at 100°C in the presence of water vapor, corresponded to a $\Delta\delta$ of 33 Hz compared to 57 Hz for pure triethanolamine. The NMR spectra of pure triethanolamine and of a triethanolamine sulfite salt are shown in Figure 3. In Figure 4 we plotted the acidity data $\Delta\delta$ and pH for a variety of samples obtained during this program as a function of the sulfur dioxide in triethanolamine. It should be noted that samples with sulfur dioxide concentrations above about 23 gms per 100 gms of amine (composition of the neutral salt is 21.5 gms per 100 gms) were obtained only with 100% sulfur dioxide, both at room temperature and at 100°C. The pH function showed a two-step pH decrease with increasing sulfur dioxide concentration with a buffer zone at pH 7.2-7.0 at a mole ratio 1 SO_2:2 TEA. The NMR data indicated a strong acidity change up to a mole ratio 1 SO_2:2 TEA, but little change

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[4] Compare C.N. Reilly, Anal Chem. 36, 1968, 1707 (1964)

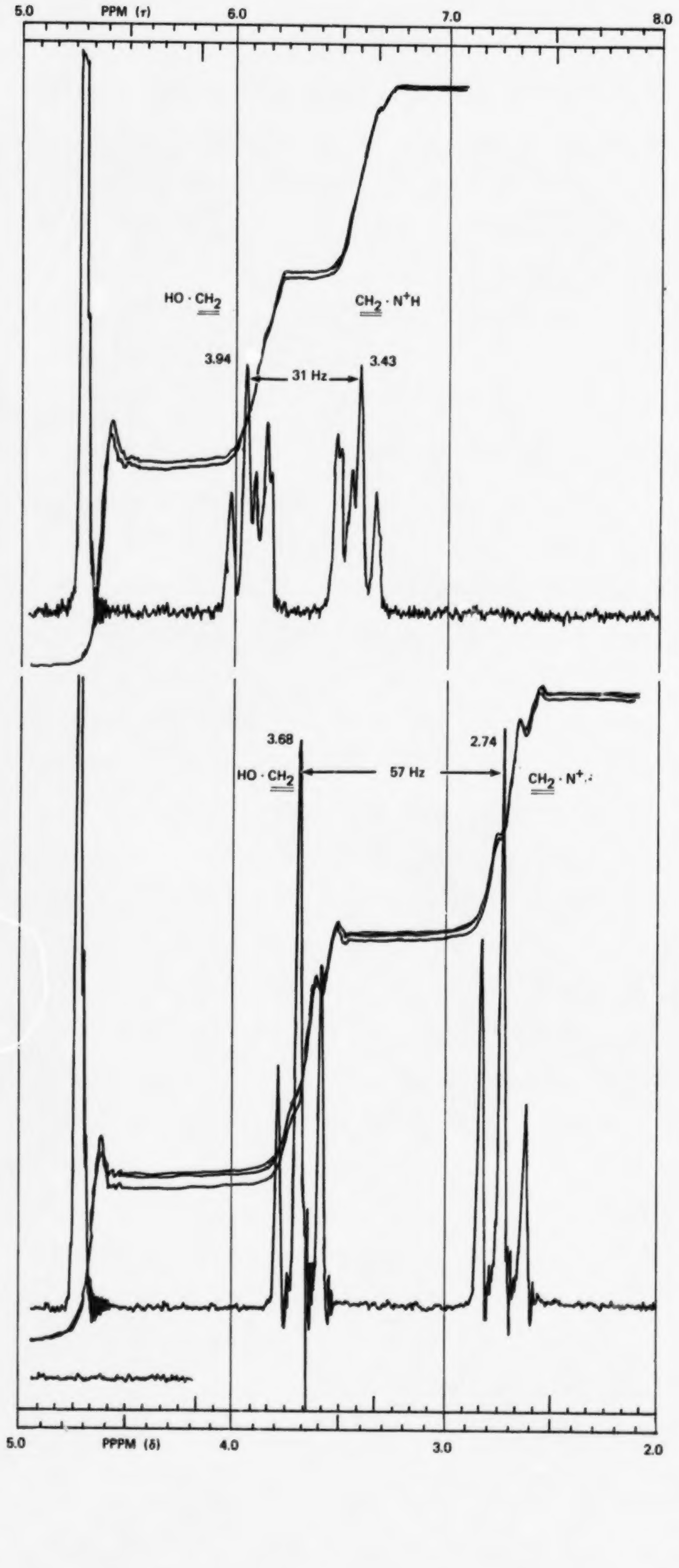

FIGURE 3 NMR SPECTRUM OF TRIETHANOLAMINE-SULFUR DIOXIDE (ABOVE)AND OF TRIETHANOLAMINE (BELOW)

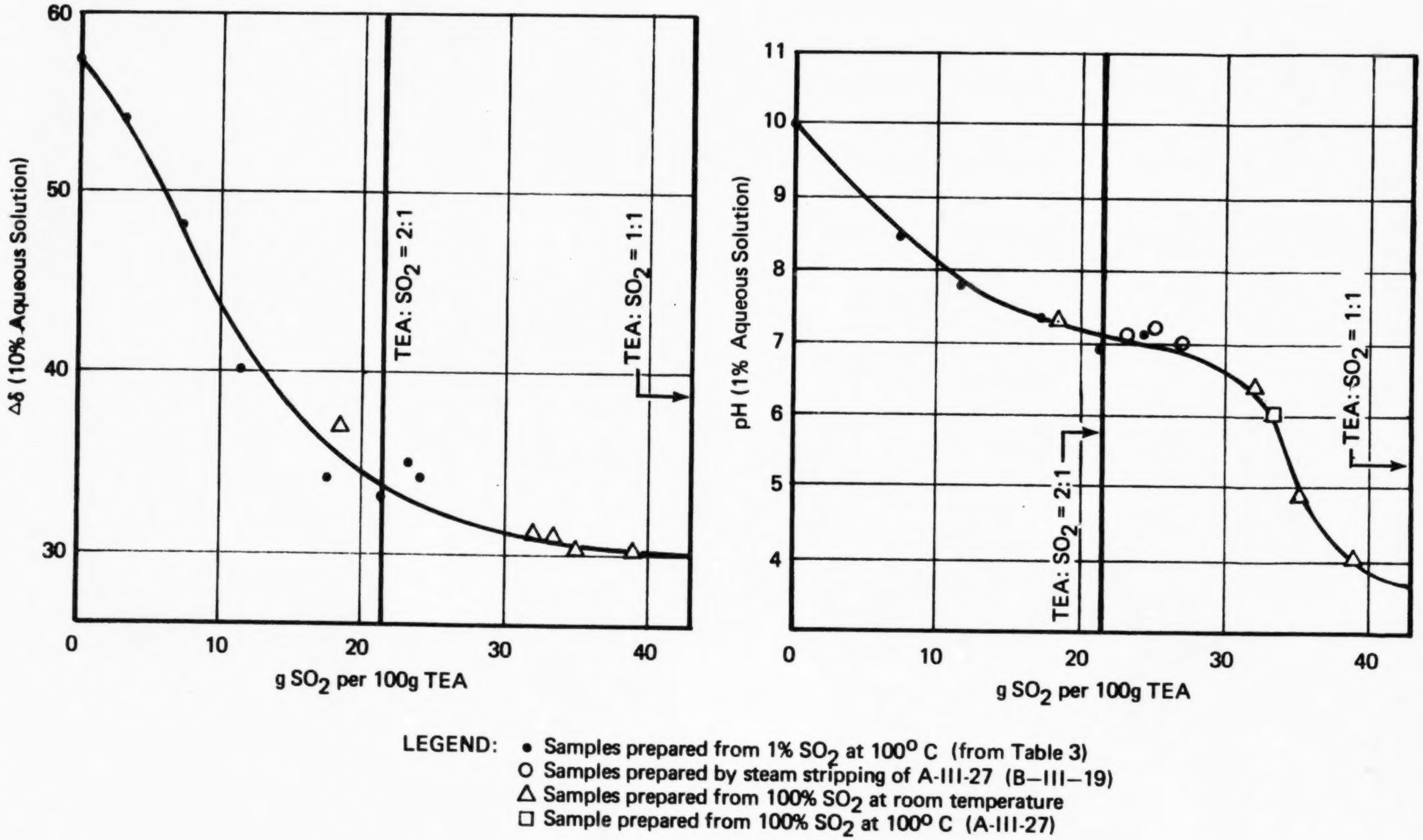

FIGURE 4 ACIDITY FUNCTIONS FOR THE SYSTEM TRIETHANOLAMINE – SULFUR DIOXIDE

subsequently. Since NMR measures the degree of protonation of the amine, there was little further shift as the neutral sulfite salt was converted to the acid salt.

4. Attempted Sulfur Dioxide Absorption from a Simulated Flue Gas

We carried out one experiment to test the sulfur dioxide absorption from a simulated flue gas at 100°C and to evaluate the chemical stability of triethanolamine under these conditions. Unfortunately the conditions of our experiment were such as to allow significant formation of sulfur trioxide and sulfuric acid mist in the gas phase. Consequently we found in the amine predominantly sulfate. The experiment and results are described below:

The gas mixture consisting of 0.3% SO_2, 0.1% NO_x, 5% O_2, 10% CO_2 and the balance N_2 was prepared by metering the gases. It was saturated with water vapor (about 10% H_2O) and contacted with the triethanolamine at a rate of 1 liter/min. The condition and results are shown in Table 4. A sample of 200 g of triethanolamine was contacted with 4000 liters of the simulated flue gas (measured dry) and a sample of 80 g of the resulting absorption product was subsequently contacted with an additional 4290 liters of the gas. The sulfur dioxide uptake per 100 g amine as a function of the volume of flue gas per 100 g of amine is shown in Figure 5. The graph shows that no saturation of the amine was reached, even though the composition of the neutral salt (mole ratio 1 SO_2:2 TEA; 21.5 g of SO_2 per 100 g of TEA) was far exceeded. Measurements of the pH in aqueous solutions of the absorption products showed strongly acidic conditions after the neutral salt composition was exceeded. The amine appeared to absorb under the test conditions about 45% of the sulfur dioxide present in the flue gas independent of the degree of amine saturation. Determinations of the sulfate in samples A-III-30-4 and -7 indicated that 73% and 78%, respectively, of the sulfur was present as sulfate. The unexpected behavior of the amine under flue gas conditions appeared to be explained by the observation of crystalline deposits in the dry flue gas lines. These deposits liberated nitrogen dioxide and sulfuric acid on addition of water and therefore appeared to be nitrosyl sulfuric acid or dini-

Table 4

Sulfur Dioxide Absorption in Triethanolamine (TEA) From Simulated Flue Gas(1)

	Flue Gas Contacted (Liters)(2) Per Sample	Flue Gas Contacted (Liters)(2) Per 100g Amine	Analysis %S	Analysis %N	g SO_2 per 100g TEA	g H_2O per 100g TEA(3)	pH (1% Solution)
1. Sample = 199.8g TEA							
A-III-30-1	1800	900	2.17	8.84	4.7	0.6	
2	2590	1300					
3	2880	1440	2.67	8.08	6.2	8.6	
4	4000	2000	2.74 SO_4: 2.04 (73% of total)	8.32	6.1	5.3	8.3
2. Sample = 80.6g A-III-30-4 (71g TEA)							
A-III-30-5	2700	5800	8.05	7.31	20.7	1.3	
6	3670	7180	8.70	7.01	23.3	4.8	
7	4290	8050	10.12 SO_4: 7.86 (78% of total)	7.04	27.0	0.0	6.2
3. Sample = 17.0g A-III-30-7 (12.5g TEA)							
8	1112	17000	12.0	7.96(4)	28.7	(-13.0)	2.9

---

(1) Flue gas composition: 0.3% SO_2, 0.1% NO_x, 5% O_2, 10% CO_2, bal. N_2

(2) Gas flow rate: 1 liter/1 minute

(3) Based on sulfur and nitrogen analysis and assming sulfur present as sulfate

(4) High nitrogen content, possibly because of condensation of nitric acid or nitrosylsulfuric acid

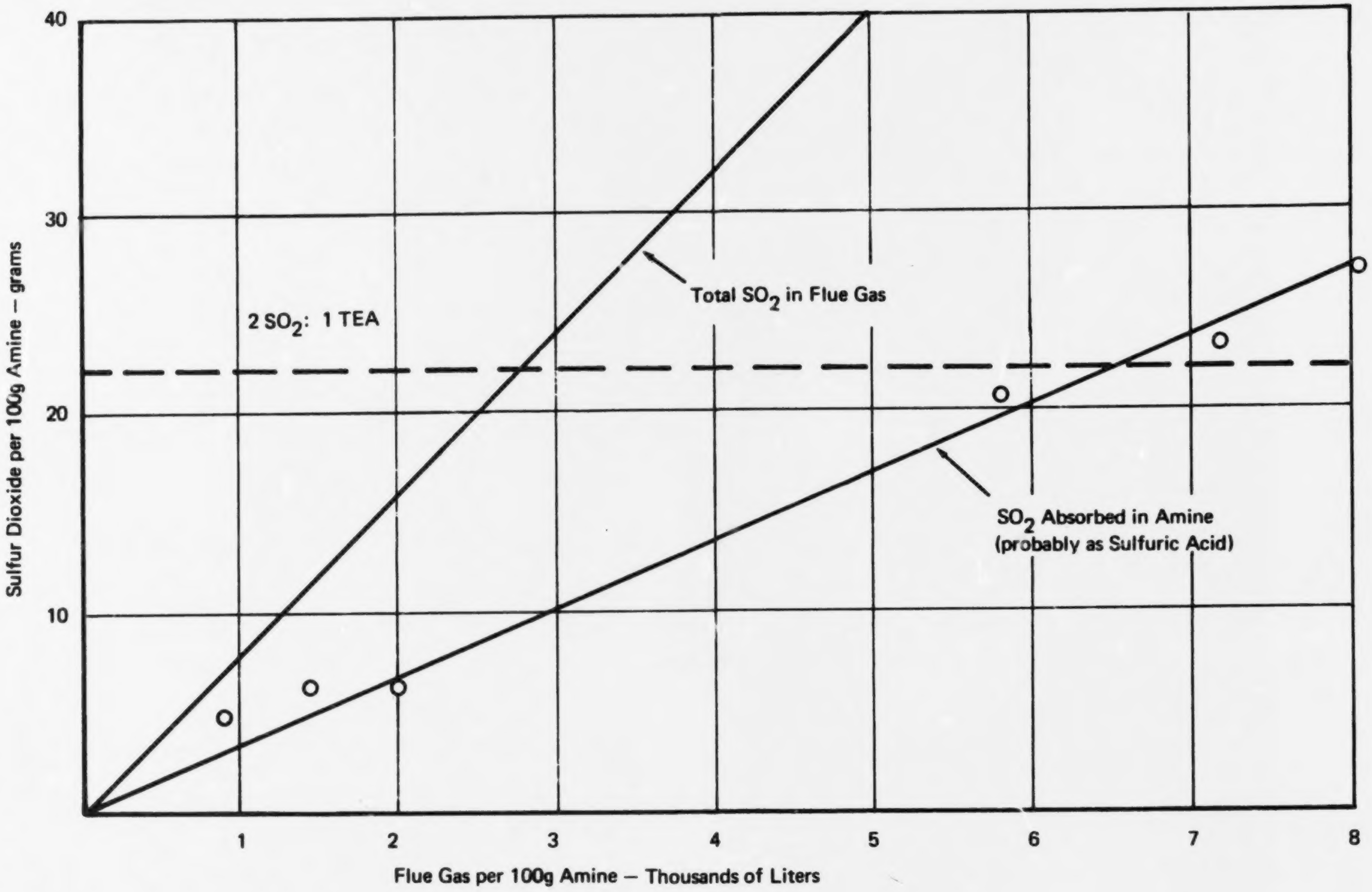

FIGURE 5 SULFUR DIOXIDE ABSORPTION IN TRIETHANOLAMINE AT 100° C FROM A SIMULATED FLUE GAS

trosyldisulfate, both of which are well known as deposits in the "chamber process" for sulfuric acid production under conditions of water deficiency.

$$NO_2 + NO + 2SO_3 \longrightarrow (NO)_2S_2O_7 \xrightarrow{+H_2O} NO + NO_2 + 2H_2SO_4$$

It thus appears that the simulated flue gas was an unstable system at the low temperature of preparation and produced sulfur trioxide or sulfuric acid in the gas phase at an appreciable rate: sulfur trioxide produced before the gas stream was saturated with water deposited as dinitrosyldisulfate or was absorbed in the water saturator. Part of the sulfuric acid was carried through the saturator to form an acid mist, further augmented by acid produced from sulfur dioxide in the wet gas stream. The sulfuric acid mist then appeared to be neutralized in the triethanolamine scrubber at 100°C. An alternative explanation for the observed results would be a catalysis of the sulfur dioxide or sulfite oxidation by the combination of nitrogen oxides and triethanolamine. We feel this to be much less likely.

The flue gas composition chosen appears to be high in nitrogen oxides and oxygen. The extent of sulfate formation might be lower if lesser concentrations of these constituents were present. Moreover, the synthetic flue gas should be maintained at a temperature of not less than 100°C. This would lower the equilibrium concentration of nitrogen dioxide. Very probably the extent of sulfate formation in the amine would be significantly lower under such conditions.

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III. CHARACTERIZATION OF AMINE SULFUR DIOXIDE ABSORPTION PRODUCTS

1. Evidence for Sulfur Dioxide Disproportionation into Di- and Polythionates at Elevated Temperatures

We suggested in Section II.3 that the absorption of sulfur dioxide in amines might be accompanied by a disproportionation of the resultant sulfite or pyrosulfite into di- and polythionates. In this section we present further evidence for this mechanism based on studies on the sulfur dioxide-amine absorption products.

During our measurements of sulfur dioxide absorption in amines at 100°C we observed a discrepancy between the analytical determination of sulfur dioxide in the amines by the usual iodometric titration method and by total sulfur determination. To investigate this phenomenon we absorbed sulfur dioxide in amines at room temperature and then held the product at 100°C over a period of time, while taking samples in intervals. The results obtained with two different samples of triethanolamine-sulfur dioxide are shown in Table 5 and Figure 6.

Sample A-III-25 was prepared in the absence of water at room temperature with 100% sulfur dioxide gas. It absorbed 18.4 gms of sulfur dioxide per 100 gms of triethanolamine, which is close to the composition of a neutral salt. The formulation as neutral salt however would require about 12 gms of water per 100 gms of amine, and the "difference analysis" data based on nitrogen and sulfur determinations showed a water content between 1.9 and 2.4 gms per 100 gms of triethanolamine. The product, therefore, could be formulated as an adduct, 2 $TEA \cdot SO_2$.

In the freshly prepared sample, practically all the sulfur dioxide could be titrated iodometrically. But the available sulfur dioxide decreased with the length of exposure of the sample to 100°C. The total sulfur analyses indicated no loss of sulfur dioxide. NMR and IR spectra did not reveal principal changes in the system, except for the appearance in the samples after 24 and 48 hours of two minor absorption bands which could be assigned to carbonyl groups and to unsaturation. This latter change was accompanied by a slight decrease in the acidity of the system according to the NMR data. It appeared to be the beginning of an oxidation of the amine by sulfur species in the system. This

Table 5

CHANGES IN THE SYSTEMS TRIETHANDAMINE - SULFUR DIOXIDE AND TRIETHANDAMINE - WATER - SULFUR DIOXIDE AT 100°C AS A FUNCTION OF TIME(1)

Time at 100°C (hrs)	Analysis(2)		Per 100g TEA		Sulfite(3)	Sulfate(4)	Sulfur On Acid Addition(5)	NMR	IR
	%N	$\%SO_2$	SO_2	H_2O	$\%SO_2$	$\%SO_2$			
Sample A-III-25:2 $TEA\cdot SO_2$									
0	7.83	15.2	18.4	2.4	14.5	trace	neg.	37	NH^+, SO_2-HSO_3
1					14.6			37	same
3					14.0	trace	neg.		
5	7.80	15.4	18.6	1.9	13.1			37	same
22	7.85	15.3	18.3	1.9	7.5				
24					6.1	3.2	pos.	40	same plus trace 1720 cm^{-1} (carbonyl) 1590 cm^{-1} (unsatur.)
48	7.80	15.1	18.2	2.3	2.8	2.8	pos.	42	
Sample A-III-26: $TEA\cdot H_2O\cdot SO_2$									
0	6.30	22.2	33.3	16.8	21.3	trace	neg.	31	NH^+, SO_2-HSO_3
1					23.3			31	same
3					16.2	trace			
5	5.60	20.6	34.7	32.5	13.9			32	same
22	6.00	20.6	32.4	24.1	8.2				
24					6.6	2.9	pos.	31	same
48	6.80	20.8	28.7	8.8	3.6	0.9	pos.	31	same

(1) The samples were prepared at room temperature with 100% SO_2

(2) Analysis by Schwarzkopf Microanalytical Laboratory

(3) By iodemetric titration

(4) This analysis includes sulfate formed during acidification and is adulterated slightly by the elemental sulfur precipitating during acidification

(5) Tests for sulfide were negative in all samples

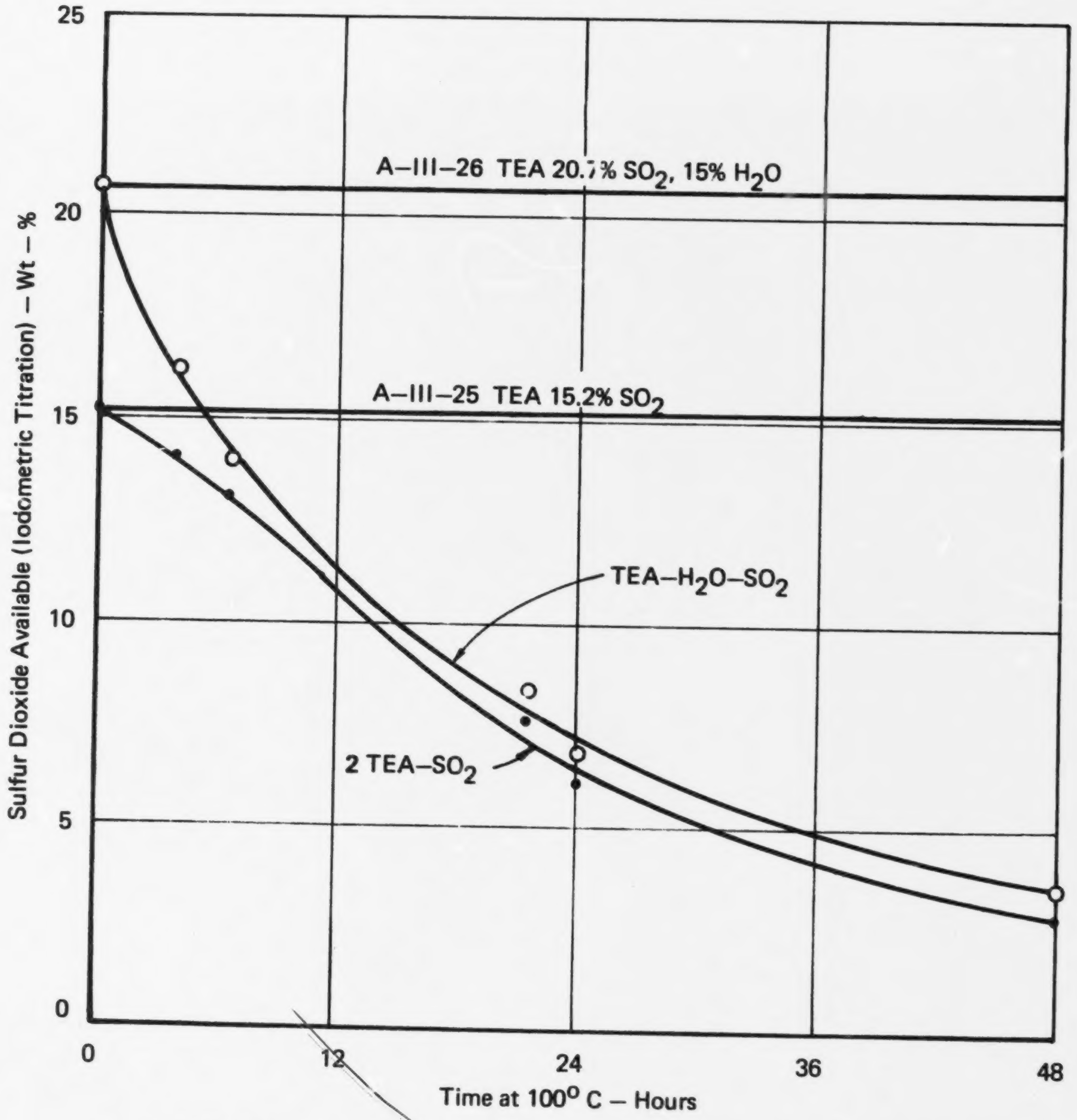

FIGURE 6 AVAILABLE SULFUR DIOXIDE IN TRIETHANOLAMINE AS A FUNCTION OF TIME AT 100° C

oxidation was not observed in the second sample (A-III-26) which had one mole of water added per mole of triethanolamine (12.1 gms per 100 gms of the amine). It absorbed about 34 gms of sulfur dioxide per 100 gms of amine during treatment with 100% sulfur dioxide at room temperature. (No effort was made to assure saturation.) The system was, therefore, more acid than the first one (compare the NMR acidity values) and its composition was between that of a neutral and acid salt; the sample crystallized on standing at room temperature to a solid with a melting point of about 56°C. The infrared absorption spectrum for this sample was practically identical with the one for the first sample prepared in the absence of water. The "difference analysis" showed wide variations in the water contents of the samples taken during the experiment. This appeared to be due to distillation of water from the sample during the period at 100°C and condensation on the cooler parts of the container.

The decrease of available sulfur dioxide in the two systems might be the result of a disproportionation of the sulfite into sulfur species of higher and lower oxidation states. Evidence for sulfur of lower oxidation states was the formation of turbidity due to elemental sulfur when acid was added to samples taken after 24 and 48 hours at 100°C. In an experiment described later in this report, a sample of triethanolamine which was saturated with sulfur dioxide at 100°C precipitated 9.3% of its contained sulfur as elemental sulfur on addition of acid. On the other hand, formation of sulfate during the reaction at 100°C appeared to be minor. In the 24 and 48 hour samples we determined about 3% (as sulfur dioxide) sulfate, which was about 20% of the contained sulfur in sample A-III-25. But the sulfate might have been formed by disproportionation after the addition of acid, which is necessary for the precipitation of sulfate as the barium salt. In addition, elemental sulfur was present in these precipitates. Other tests showed that no sulfide was present in any of the samples. However, it will be shown later in this report that boiling of an aqueous solution of a triethanolamine-sulfur dioxide sample prepared at 100°C in the presence of lime will liberate about 3.4% of the contained sulfur as hydrogen sulfide.

The decrease in available sulfur dioxide also was observed in tetraethylene pentamine (TEPA). A sample of this amine, containing about 10% water was treated with 100% sulfur dioxide at room temperature. A solid precipitate formed, which was then separated from excess amine and held at 100°C for 48 hours in the molten state. The results of a total sulfur analysis and determinations of available sulfur dioxide are shown in Table 6.

We conclude from the evidence that the sulfur species formed in the amine systems at 100°C could consist of di-, tri, and pentathionates, as well as some thiosulfate. Some of the reactions proceeding might be represented by the following equations:[4]

$$\underset{\text{sulfite}}{4SO_3^{2-}} + 4H^+ \xrightarrow{-2H_2O} \underset{\text{pyrosulfite}}{\overset{+4}{2S_2O_5^{2-}}} \longrightarrow \underset{\text{dithionate}}{\overset{+5}{S_2O_6^{2-}}} + \underset{\text{dithionite}}{\overset{+3}{S_2O_4^{2-}}}$$

$$S_2O_4^{2-} + 2\ OH^- \longrightarrow \underset{\text{sulfoxylate}}{\overset{+2}{(SO_2^{2-})}} + \overset{+4}{SO_3^{2-}} + H_2O$$

$$2(SO_2^{2-}) + 2H^+ \longrightarrow \underset{\text{thiosulfate}}{\overset{+2}{S_2O_3^{2-}}} + H_2O$$

$$(SO_2^{2-}) + 2S_2O_3^{2-} + 4H^+ \longrightarrow \underset{\text{pentathionate}}{\overset{+2}{S_5O_6^{2-}}} + 2H_2O$$

$$(SO_2^{2-}) + 2SO_3^{2-} + 4H^+ \longrightarrow \underset{\text{trithionate}}{\overset{+3.3}{S_3O_6^{2-}}} + 2H_2O$$

These reactions produce primarily dithionate in addition to tri- and penta-thionate and in more alkaline solutions thiosulfate can also be present.

The chemistry of sulfur and its acids has advanced significantly

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[4] Compare: Holleman-Wiberg, Lehrbuch der Anorganischen Chemie, 57-70 edit. Walter De Gruyter & Co. Berlin 1964, p 213-215.

Table 6

Decrease of Available Sulfur Dioxide in Tetraethylenepentamine (TEPA) at 100°C. (Sample A-VII-28)*

Total sulfur		16.0% SO_2
By Iodine Titration:		
	as is	13.6%
	24 hrs. 100°C	6.0%
	48 hrs. 100°C	4.9%

* Sample prepared by absorption of 100% SO_2 in TEPA-10% H_2O at room temperature.

in the last ten years especially through the work of Max Schmidt[5] at the University of Munich, Germany (now at the University of Marburg, Germany) and the earlier work of F. Feher at Marburg.

The major conclusions from their work are as follows: Thionates ($S_xO_6^{2-}$) have the structures of sulfane disulfonates ($^-O_3S\text{-}S_x\text{-}SO_3^-$; x = 1 to 12 and together with sulfane monosulfonates ($^-S_xSO_3^-$) and sulfanes (S_x^{2-}) must be considered derivatives of elemental sulfur (S_8) with straight chains of sulfur-sulfur-bonds. The valence state of sulfonate sulfur is formally +5, the one of the sulfur in the sulfur chain is 0.

Certain nucleophilic agents, such as sulfite, cyanide and arsenite can degrade sulfane derivatives (as well as elemental sulfur) into smaller fragments and this reaction might be useful for adjusting the composition of the amine-sulfur dioxide absorption product. For example the sulfite degradation of sulfane disulfonates proceeds quantitatively as follows:

$$S_xO_6^{2-} + (x-3)SO_3^{2-} \longrightarrow S_3O_6^{2-} + (x-3)S_2O_3^{2-}$$

Accordingly, the end products of this reaction are trithionate and thiosulfate. In the amine-sulfur dioxide system we have in addition dithionate ($S_2O_6^{2-}$), which is formally a member of the sulfane disulfonate series, but differs in its characteristic reactions. Its alkali salts decompose at 260°C according to:

$$S_2O_6^{2-} \longrightarrow SO_4^{2-} + SO_2$$

The various sulfur species can be identified and quantitatively determined by chemical methods. A very complicated system of qualitative and quantitative determination was worked out as early as 1936. The best modern method is separation on an anion exchange column.

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[5] A summary of the newer findings is given by Max Schmidt in Inorganic Polymers, Academic Press, 1967, Edited by F.G.A. Stone and W.A.G. Graham.

2. Thermal Stabilities of Amine-Sulfur Dioxide Systems

The results of thermogravimetric and differential thermal analysis (TGA and DTA) for four amine-sulfur dioxide systems are shown in Figures 7 and 8. All samples were prepared at 100°C from a wet gas containing 1% sulfur dioxide (see Table 1).

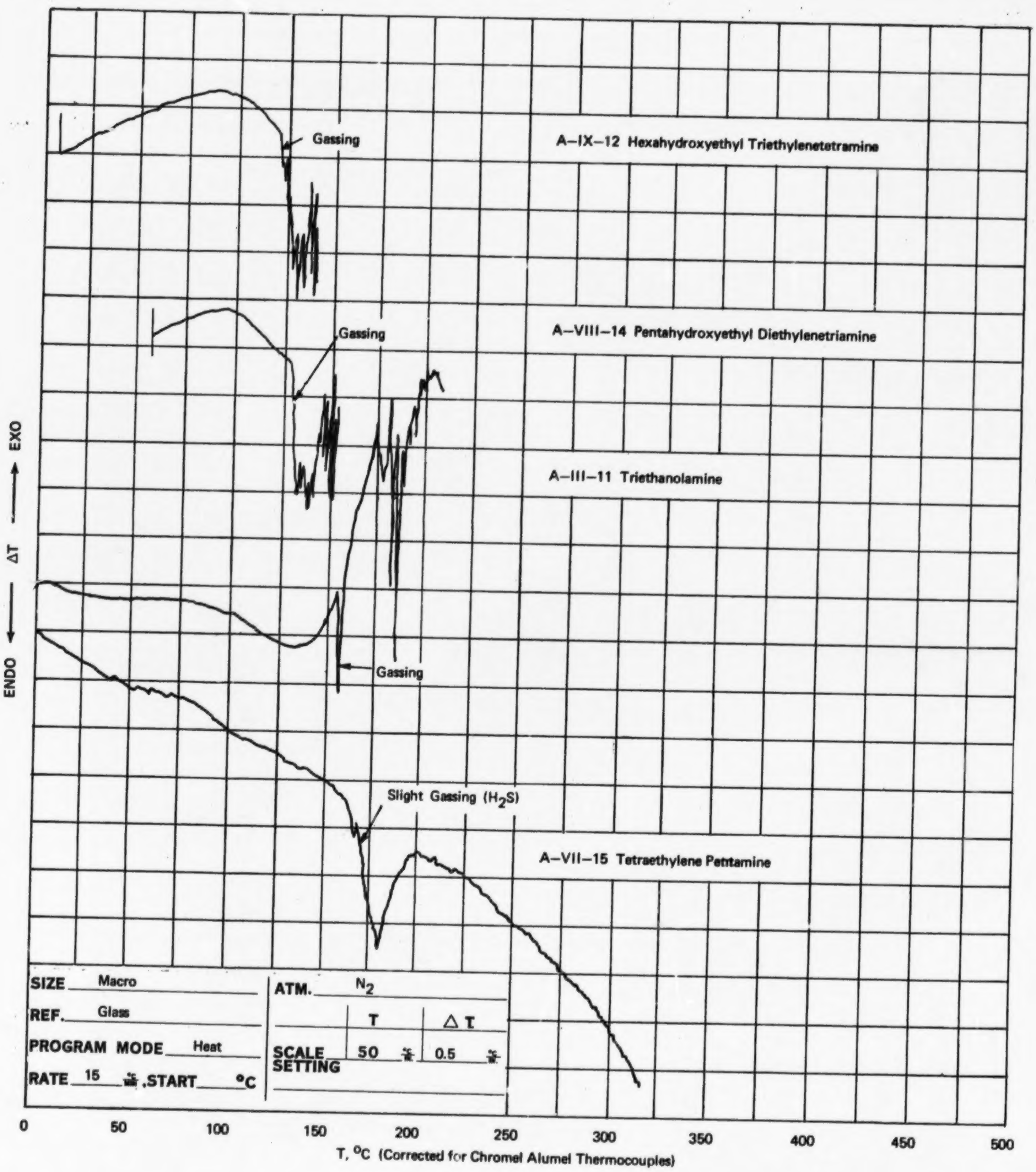
The DTA curves indicate that in triethanolamine and the two ethoxylated amines decomposition began at 125 - 130°C. The reactions were marked by a darkening of the product, gas evolution and unpleasant odor. The reaction of triethanolamine specifically appeared to be exothermic and produced a black polymeric tar. Tetraethylenepentamine - sulfur dioxide showed no change up to 160 - 170°C; it then turned dark green and liberated hydrogen sulfide becoming finally clear yellow at a temperature above 200°C.

The TGA curves show no significant inflections which could reflect loss of sulfur dioxide or of reaction products at the decompositon temperatures indicated by DTA. The curves represent more or less the decomposition and/or vaporization of the entire samples. In Table 7 we have summarized the vaporization losses for each sample as taken from Figure 7. It can be seen that the triethanolamine - sulfur dioxide sample was significantly more volatile than the three others.

A few tests were carried out to evaluate the thermal stabilities of the selected amines in the absence of sulfur dioxide both in an inert gas and in air. The results are shown in Table 8. All amines were stable o at least 150°C under argon. Triethanolamine was stable to about 200°C under argon, but showed signs of decomposition at 150°C in air.

The reactions which occurred between amines and sulfur dioxide at elevated temperatures were limiting the useful temperature range of the amine as a regenerative absorbent. It was therefore desirable to gain some knowledge of the type of reactions occurring in order to devise means of preventing them or select other amines which lacked the ability to undergo these reactions. This program did not include a detailed study of such reactions, but some observations provide a little insight into their nature.

First, as indicated earlier, a partial reaction between sulfur



SIZE Macro

REF. Glass

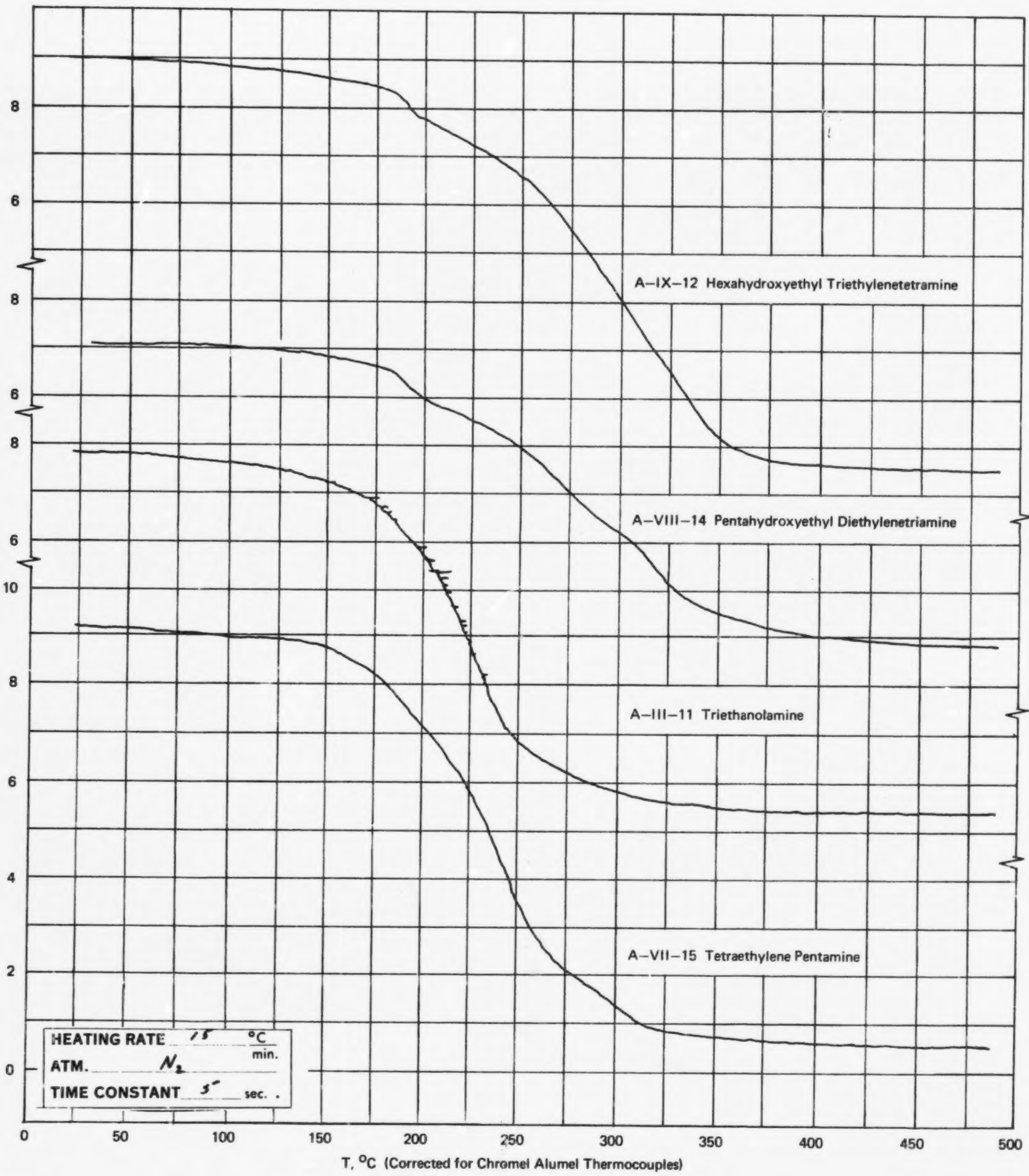
PROGRAM MODE Heat

RATE 15 °C/min, START °C

ATM. N_2

	T	ΔT
SCALE SETTING	50 °C/in	0.5 °C/in

FIGURE 7 DIFFERENTIAL THERMAL ANALYSIS OF AMINE – SULFUR DIOXIDE SYSTEMS



HEATING RATE 15 °C/min.

ATM. N_2

TIME CONSTANT 5 sec.

FIGURE 8 THERMOGRAVIMETRIC ANALYSIS OF AMINE – SULFUR DIOXIDE SYSTEMS

Table 7

Weight Losses of Selected Amine-Sulfur Dioxide Systems in Thermogravimetric Analysis

(Heating Rate 15°C per min)

Sample No	Amine	% SO_2	Percent Weight Loss		
			100°C	200°C	250°C
A-VII-15	Tetraethylene pentamine	10.4	3.1	5.3	41.9
A-III-11	Triethanolamine	17.9	1.2	14.1	76.9
A-VIII-14	Pentahydroxyethyl diethylenetriamine	23.1	1.2	4.2	29.6
A-IX-12	Hexahydroxyethyl triethylenetetramine	15.8	2.1	4.3	27.7

Table 8

Stability Screening Tests

Argon blanket, 150°C, 24 hr-tests:

Triethanolamine	no change
Tetraethylenepentamine	no change
Pentahydroxyethyl diethylenetriamine	dark brown
Hexahydroxyethyl triethylenetetramine	light brown

Triethanolamine - 24 hr-tests:

	Argon purge	Air purge
100°C		no change
150°C	no change	dark brown
200°C	yellow	
250°C	dark brown	

species and the amine appeared to take place at 100°C in the absence of water. It produced unsaturation and carbonyl groups in the amine as indicated by IR spectra. This reaction might be caused by sulfoxylate, SO_2^{2-}, which is an unstable, oxidizing intermediate of the disproportionation reaction in aqueous systems. In a water deficient system at 100°C it might accumulate according to:

$$2SO_3^{2-} + SO_2 \longrightarrow S_2O_6^{2-} + SO_2^{2-}$$

The oxidation produces water which is immediately consumed in further disproportionation reactions. The presence of sufficient water in the systems prevents the oxidation reaction.

Further reactions appeared to occur in triethanolamine and ethoxylated amines around 130°C. This reaction seemed to be independent of the water present and involved formation of organic sulfur containing compounds, some of which were volatile and very malodorous. In attempts to strip sulfur dioxide from triethanolamine at 150°C by steam or nitrogen purging (compare Table 13 in Section IV), hydrogen sulfide as well as two other volatile components were found by gas chromatography of the gas phase and a drop of yellow oil was recovered by condensation. The IR spectrum of this oil could not be identified. The major product was a tar-like residue. Samples of this residue also were obtained in the screening tests for sulfur dioxide solubilities at 100°C (Table 1). They showed very high nitrogen values, indicating a loss of a moiety low in nitrogen. The NMR spectrum of this reaction product showed only the signals for pure triethanolamine, probably because of the water insolubility of the polymeric products and organic sulfur compounds. The infrared spectrum showed few changes other than the appearance of absorption bands characteristic for carbonyl groups and unsaturation. A cursory inspection of the literature showed that many reactions of organic compounds including amines with sulfur dioxide, elemental sulfur, ammonium sulfide, and thiosulfate and other sulfur species have been reported, often indicating formation of tar-like polymeric products, as in our system. No specific reference to reactions of sulfur species with triethanolamine was found.

An attempt was made to fractionate the black residue obtained in a stripping test (B-III-12, Table 13 in Section IV) in order to evaluate how much unreacted triethanolamine could be recovered. The original sample, before heating to 150°C, contained 18.2 gms SO_2 and 2 gms water per 100 gms of amine, i.e. somewhat less than required for the composition of a neutral salt. The results of the fractionated vacuum distillation are summarized in Table 9. The main fraction between 162 and 175°C at 1 mm Hg consisted primarily of triethanolamine with some impurities according to the IR spectrum. The forerun and after-run consisted primarily of other compounds which might include glycol, or morpholine structures, or other cyclic nitrogen compounds according to IR and NMR data. Twenty-five percent of the sample remained as a black, very hard polymeric product in the still bottom. We conclude that about 50% of the original triethanolamine was recovered in this fractional distillation, while about 50% of the amine was destroyed during the attempted thermal stripping. This is agreeable with the roughly 43 mole-% sulfur dioxide in the triethanolamine sample before the decomposition.

Tetraethylenepentamine appeared to be more stable at high temperatures toward sulfur dioxide than did triethanolamine. The differential thermal analysis (DTA) of the sulfur dioxide - tetraethylenepentamine showed an endothermic reaction with formation of hydrogen sulfide at 170 - 200°C. It appeared that this reaction might involve the further disproportionation of the sulfur species into sulfide and sulfate according to the overall equation:

$$4SO_3^{2-} \longrightarrow S^{2-} + 3SO_2^{2-}$$

An experiment therefore was carried out to quantitatively determine the end products of the reaction. A total of 39.5 g of tetraethylenepentamine containing 21.8% sulfur dioxide and 16.4% water was heated to 200°C for 3 hours. Hydrogen sulfide was swept from the reactor by a stream of dry nitrogen and absorbed in a solution of lead acetate. The lead sulfate recovered (26.2g) accounted for 82% of the

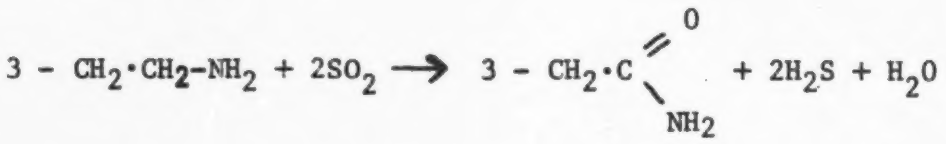
TABLE 9

Vacuum-Fractionation of Triethanolamine - Sulfur Dioxide Residue After Thermal Stripping

(Sample B-III-12)

Temperature Range	Weight(g)	Percent of Total Sample	Remarks (IR, NMR)
140-162°C/1mm Hg	2.2	10.4	NMR: about 50% TEA, $\Delta\delta$ = 56. IR: carbonyl groups, unsaturation. Incompletely soluble in water.
162-175°C/1mm Hg	11.6	54.6	NMR: mostly TEA, $\Delta\delta$ = 56. IR: carbonyl groups. Incompletely soluble in water.
175-186°C/1mm Hg	2.1	9.9	NMR: no TEA present IR: morpholine (?), glycol (?).
Residue	5.3	24.9	black solid polymer
Total	21.2	99.8	insoluble in water
Original Sample	21.3	100.0	black, viscous liquid

total sulfur present. The sulfate in the light brown amine residue was neglible, amounting to less than 2% of the total sulfur. We must therefore conclude that the amine had reduced essentially all of the sulfur present to hydrogen sulfide. The infrared spectrum of the amine oxidation product indicated that amide groups were formed in this process. The reaction might be as follows:



$$3 - CH_2\cdot CH_2\text{-}NH_2 + 2SO_2 \longrightarrow 3 - CH_2\cdot C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown NH_2} + 2H_2S + H_2O$$

The reaction could be exploited for a cyclic process if it were possible to regenerate the original amine by reduction of the amide. A brief review of the chemistry of amides suggests that hydrogen reduction in the presence of catalysts might be difficult because of possible catalyst poisoning by sulfur compounds. But it might be possible to replace the amine as reducing agent by other low cost reducing agents, such as hydrogen, carbon monoxide or methane; other useful reducing agents might be methanol, ammonia or catalytic systems using any of these reagents. The reaction should be accomplished below 170°C. Because of its weakly acidic properties, hydrogen sulfide is easily desorbed thermally from the amine.

IV. THE DESORPTION OF SULFUR FROM AMINES

1. Desorption by Superheated Steam

Table 10 gives results of screening experiments using superheated steam to desorb sulfur dioxide from amines (the samples of amine-sulfur dioxide were obtained in the sulfur dioxide absorption screening, Table 1, Section II). The analytical data were computed from total sulfur and nitrogen determinations; the water content was obtained by difference, and assuming no decomposition of the amine or presence of impurities, (and its accuracy, therefore, is very limited). The data show that the desorption of about 60% of the sulfur is feasible at 150°C for triethanolamine and the two ethoxylated amines and at 200°C for tetraethylenepentamine. Qualitative observations, however, indicated that the desorbed material contained malodorous, organic compounds as well as hydrogen sulfide and sulfur dioxide. The residual products were generally discolored and contained high percentages of water. (Only exception: tetraethylenepentamine at 200°C was a clear yellow, aqueous solution.)

One experiment was designed to evaluate the feasibility of sulfur dioxide absorption and desorption (cycling) of triethanolamine based on absorption from a 1% sulfur dioxide gas at 100°C and desorption by a steam and nitrogen purge at 150°C. The results are summarized in Table 11; they demonstrate that thermal desorption causes decomposition reactions which produce hydrogen sulfide and organic sulfur compounds.

The overall absorption efficiency to saturation of the amine was 61.5% (at an average gas flow rate of 1 liter per minute and gas dispersion by a fritted glass sparger). Steam desorption removed 15% of the sulfur. The subsequent nitrogen purge was designed primarily to remove the retained water from the amine; substantial decomposition took place during this process and resulted in an additional loss of 13.5% of the contained sulfur according to the analysis of the amine. The desorbed gases were swept through a condenser and a caustic scrubber. Elemental sulfur (from hydrogen sulfide and sulfur dioxide) precipitated in the condenser and was recovered and recrystallized from carbon disulfide. The caustic solution was titrated for its combined content of sulfur

Table 10

SULFUR DIOXIDE DESORPTION BY STEAM STRIPPING (SCREENING)

Experiment No.	Condition		Amine Analysis					% Desorption
			g SO_2 per 100g Amine			g H_2O per 100g Amine		
	Temp. (°C)	Durat. (hrs.)	Before	After	Diff.	Before	After	
Triethanolamine								
B-III-1/16	150	2	24.0	19.9	4.1	12.1	66.3	17.1
B-III-2.16	150	2	24.0	10.3	13.7	12.1	36.7	56.2
B-III-5/11	150	5	23.1	11.0	12.1	6.2	19.6	52.5
B-III-8/11	200	5	23.1	9.1	14.0	6.2	24.0	60.6
Tetraethylenepentamine								
B-VII-3/15	150	2	15.9	16.5	(-0.6)	37.0	64.7	0
B-VII-6/15	150	5	15.9	12.9	3.0	37.0	117.5	18.9
B-VII-9/9	200	5	70.0	25.1	44.9	19.9	74.2	64.1
Pentahydroxyethyl triethylenetetramine								
B-VIII-4/14	150	2	27.1	24.8	2.3	(-9.6)(1)	194.0	8.5
B-VIII-7/14	150	5	27.1	10.0	17.1	(-9.6)(1)	39.2	63.2
B-VIII-10/14	200	5	27.1	10.9	16.2	(-9.6)(1)	6.7	59.9
Hexahydroxyethyl diethylenetriamine								
B-IX-11/10	150	5	23.5	9.6	13.9	(-5.6)(1)	(-6.9)(1)	59.2

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(1) The minus values are a consequence of the high nitrogen for the incompletely ethoxylated amines.

Table 11

ATTEMPTED SULFUR DIOXIDE ABSORPTION AND DESORPTION IN TRIETHANOLAMINE

(Exp. No. D-III-1)

			Composition (g per 100 g amine)		% Sulfur	NMR Acidity (Δ δ)
			SO_2	H_2O		
Absorption:						
1.13 % SO_2, 10% H_2O in N_2 100°C, 24 hours.(1)			21.4	4.4	100	35
Desorption:						
Steam	150°C	3 hours	18.9	15.9		40
		7 1/2 hours	18.9	13.8		43
		9 1.2 hours	18.2	15.7	15.0	44
N_2	150°C	2 hours	14.1	-1.1	28.5	48
Sulfur Recovery						
SO_2 + H_2S in absorber: 2.3 gms (expressed as SO_2)					10.8	
Elemental sulfur: ∿0.5 gms (about 1.0 gms expressed as SO_2)					4.7	
Total sulfur recovered					15.5	
Unaccounted sulfur (volatilized organic sulfur compounds)					13.0	

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(1) Total gas volume was 1430 liters (46.5 gms SO_2); 133.8 gms TEA absorbed 28.6 gms SO_2 or 61.5% of total SO_2 in gas.

dioxide and hydrogen sulfide. The total sulfur recovery amounted to 15.5% of the sulfur contained in the amine sample. The unaccounted sulfur (13%) is believed to have volatilized in the form of organic sulfur compounds, which may have been absorbed by the caustic solution, but could not be titrated with iodine.

The NMR acidity data for the system indicated a total loss in acidity in the stripping process as is consistent with a loss of about 12-13 gms of sulfur dioxide per 100 gms of the amine, or about 60% sulfur desorption (based on Figure 4, Section II). This is not in agreement with the observed desorption of 28.5% of the sulfur. The low acidity appears to be caused by the formation of organic nonpolar, polymeric and/or nonvolatile, water insoluble sulfur compounds from part of the triethanolamine leaving a water soluble fraction consisting predominantly of more basic triethanolamine.

Another experiment was carried out to evaluate the feasibility of steam stripping sulfur dioxide at temperatures below the decomposition of the triethanolamine-sulfur dioxide absorption product. The results of this experiment are shown in Table 12 and Figures 9 and 10. The sample used in this experiment was prepared by absorption of 100% sulfur dioxide in triethanolamine containing 12% water at 100°C; it took up about 77 mole - percent sulfur dioxide, i.e. a composition between a neutral and an acid salt. Desorption with 110-120°C steam over 19 hours brought down the sulfur content to a composition slightly in excess of a neutral salt. This is consistent with the earlier reported maximum absorption capacity at 100°C for low partial pressure (1%) sulfur dioxide. The pH of the system (in about 1% aqueous solution) increased from 6.0 to 7.1. (Compare Figure 9.)

The experiment was carried out by introducing steam through a fritted glass sparger into the sample at an average rate of 29 gms per hour. The exit steam was condensed and collected in a caustic solution. The sulfur dioxide in each fraction was determined iodometrically. Figure 10 (sulfur dioxide per liter condensed steam as a function of the sulfur dioxide concentration in the amine) shows the decrease in the rate of sulfur dioxide desorption as the composition of the amine system

Table 12

SULFUR DIOXIDE DESORPTION BY STEAM AT 110°-120°C FROM TRIETHANOLAMINE SAMPLE A-III-27*.

(Exp. B-III-19)

Duration (hrs.)	Water Condensed		Sulfur Dioxide Recovered		Sulfur Dioxide in Amine		Amine Analysis (g/100g amine)		pH
	Cumulative (liters)	Per Interval (liters)	Per Interval (gms)	Rate (gms/liter)	Per Sample (gms)	Per 100g Amine (gms)	SO_2	H_2O	(1% Solution)
0					22.2	33.3	33.3	17.3	6.0
4	1.0	1.0	3.55	3.55	18.6	27.9	27.9	79.5	
6 1/2	1.69	0.69	0.70	1.01	17.9	26.8			7.0
9 1/2	2.54	0.85	0.52	0.61	17.4	26.1	23.9	39.6	
11 3/4	3.24	0.70	0.62	0.89	16.8	25.2			7.2
13 1/2	3.79	0.55	0.34	0.63	16.3	24.4	22.4	27.2	
16	4.59	0.80	0.18	0.22	16.1	24.1			7.1
19	5.50	0.91	0.24	0.27	15.9	23.8	23.5	39.5	
Caustic scrubber			0.11						
			Total 6.26						

*Sample prepared with 100% SO_2 at 100°C; sample size 100.6 gms.

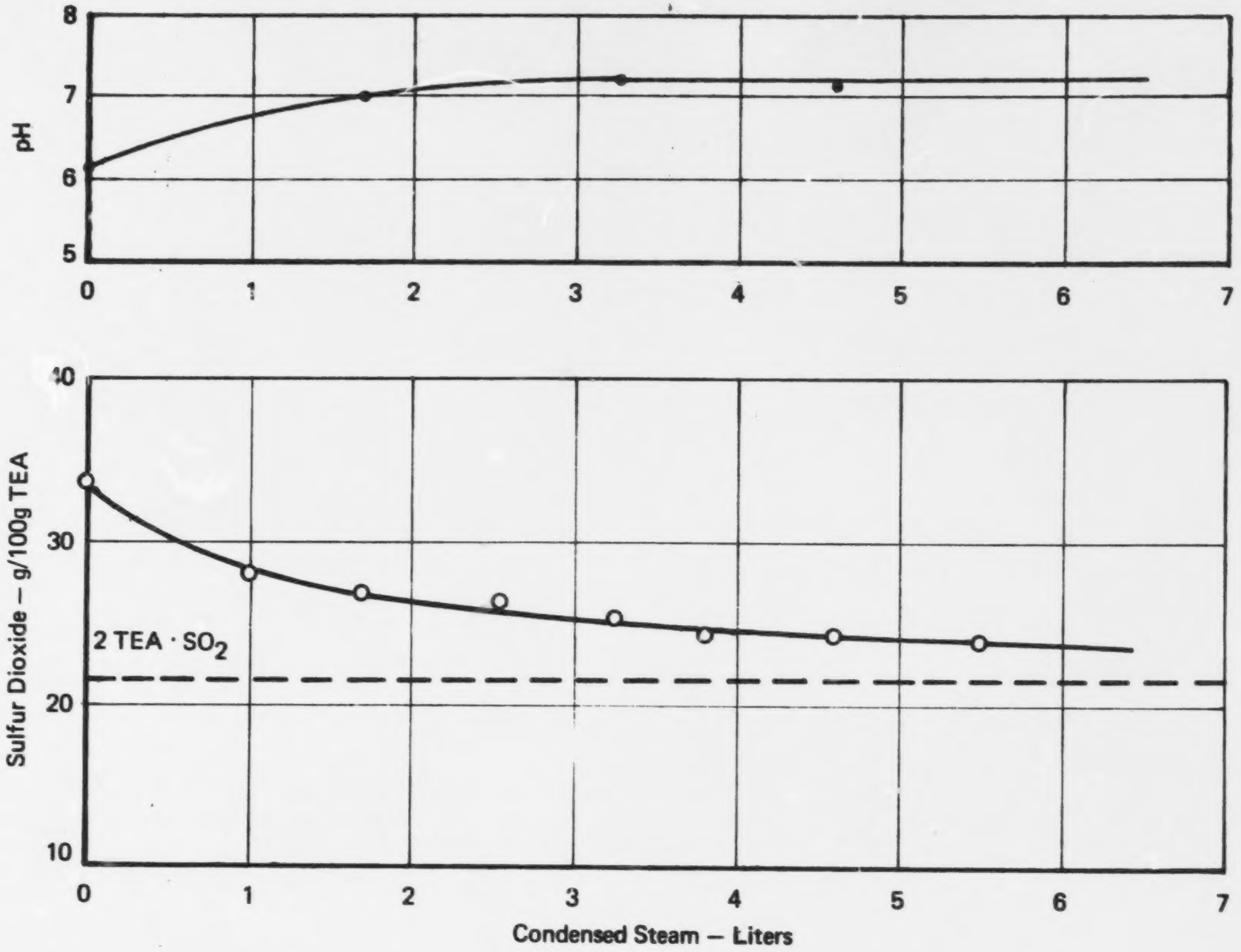

FIGURE 9 SULFUR DIOXIDE DESORPTION BY STEAM AT 110–120° C FROM TRIETHANOLAMINE SAMPLE A–III–27

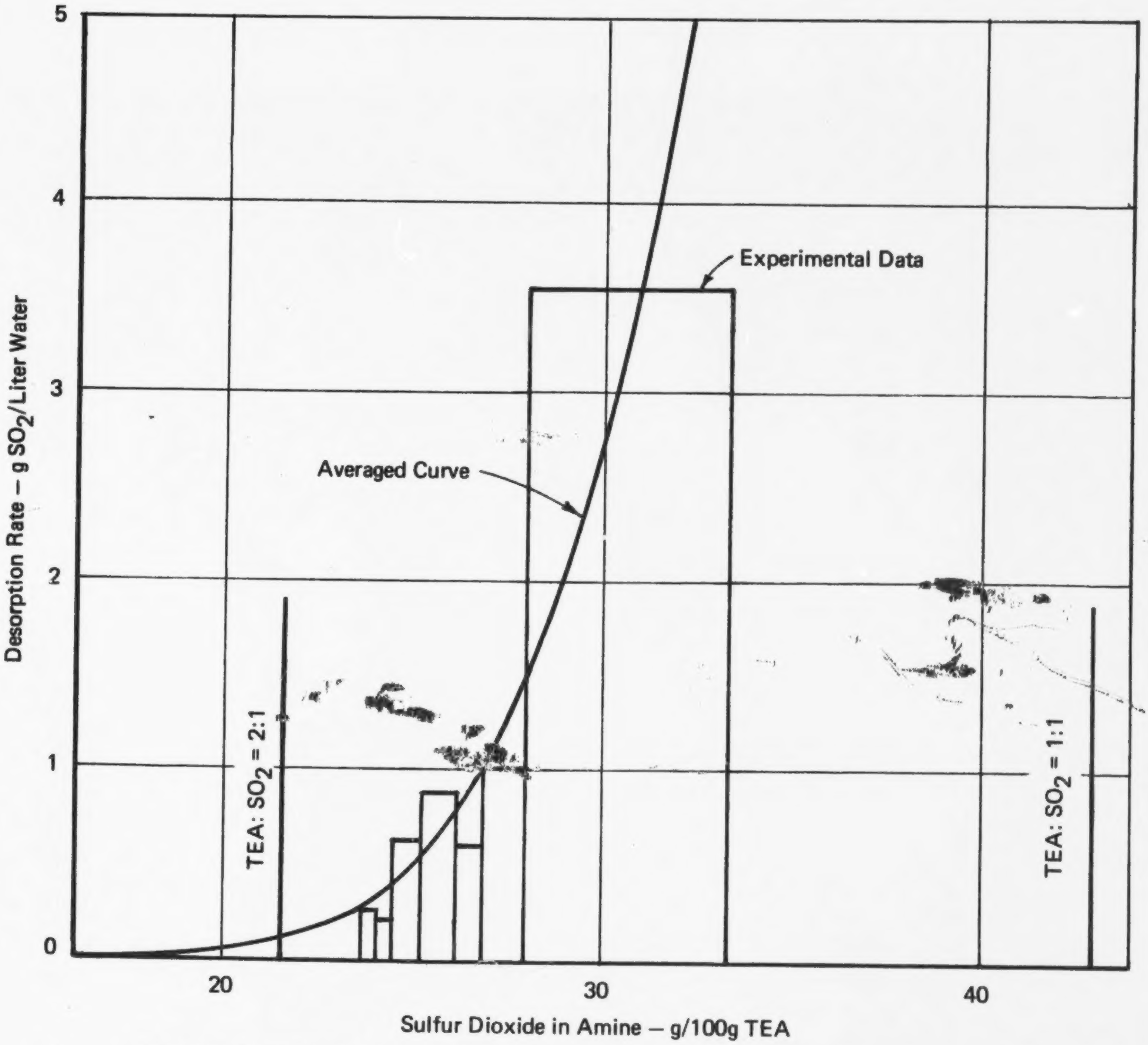

FIGURE 10 RATE OF SULFUR DIOXIDE DESORPTION BY STEAM AT 110–120°C AS A FUNCTION OF THE SULFUR DIOXIDE IN TRIETHANOLAMINE

approached the neutral salt.

Several conclusions can be drawn from the results of this experiment. First, sulfur dioxide absorbed in excess of the composition of a neutral salt at 100°C from 100% sulfur dioxide gas can be desorbed at 100°C or above by lowering the sulfur dioxide partial pressure. This might indicate either that a reversible equilibrium exists between the disproportionation products and sulfur dioxide at the acid pH or that sulfur dioxide absorbed at neutral or acid pH does not undergo the same disproportionation reaction as sulfur dioxide absorbed at a more basic pH. Second, as a whole the system appears to behave like an aqueous sulfite/bisulfite system. However, in order to utilize the amine as cyclic system at the high temperature it would be required that the acid salt forms at 100°C from a low partial pressure sulfur dioxide gas. This is not the case in the presence of moisture; some results, however, indicate that it is possible in the absence of moisture in the gas (Table 1, Section II). The dry absorption involves side reactions which have not been completely elucidated. The steam desorption of a dry absorption product was not attempted during this work, since a process requiring a dry stack gas did not appear attractive. Finally, the results shown in Figures 8 and 9 suggest that the sulfur dioxide desorption under these conditions was extremely sluggish. The average steam requirement in the experiment was 1100 lbs per lb. of sulfur dioxide and at the maximum (initial) desorption rate the required steam was 280 lbs/lb SO_2.

2. Evaluation of Desorption Techniques

A number of potential desorption techniques were evaluated as part of an effort to find an acceptable method. Table 13 summarizes experiments which were performed with amine-sulfur dioxide samples prepared at room temperature and Table 14 gives experiments with samples prepared at 100°C. The results in Table 13 demonstrate the distillation with acid (sulfuric acid) and precipitation by aqueous lime slurry are feasible methods for the regeneration of amine and recovery of the sulfur values from room temperature amine-sulfite salts. Thermal methods, involving inert gas or steam purging, or reduced pressure caused the decomposition

Table 13

SULFUR DESORPTION FROM TRIETHANOLAMINE - SULFUR DIOXIDE PREPARED AT ROOM TEMPERATURE. (Samples A-III-25 and A-III-26)(1)

Experiment No	Charge (g)	Technique	Weight Loss (%)	% Sulfur Recovered(2)	Remarks
B-III-12	110.1 A-III-25	N_2 - purge to 155°C	n.a	35.3	Volatiles: H_2S + SO_2 + H_2O + thio= compounds. Black malodorous residues.
B-III-13	99.4 A-III-25	N_2 - purge to 168°C	11.8	15.3	
B-III-14	125.5 A-III-25 100. H_2O	Steam distillation to 150°C	10.0	5.3	
B-III-15	99.3 A-III-25	Reduced pressure distillation to 180°C	22.3	30.0	
B-III-16	120.6 A-III-26	Reduced pressure distilation to 160°C	22.0	40.0	
B-III-17	125.5 A-III-25 50 H_2O 100 H_2SO_4 (1:1)	Distillation with acid to 150°C	n.a.	101.0	Volatile: SO_2 only. Colorless residue
B-III-18	125.2 A-III-25	Refluxing with aqueous lime slurry, filtration, distillation to 150°C	n.a.	91.7	

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(1) Sample A-III-25: 18.2 g SO_2, 2.0 g H_2O in 100 g TEA

Sample A-III-26: 32.0 g SO_2, 12.1 g H_2O in 100 g TEA

(2) Based on iodometric determination of SO_2 + H_2S collected in caustic scrubber

Table 14

SULFUR DESORPTION FROM TRIETHANOLAMINE - SULFUR DIOXIDE PREPARED AT ROOM TEMPERATURE. (Sample A-III-27)(1)

Exp. No.	Experimental Conditions	Sample Size		Sulfur Recovered		
		Weight (g)	g SO_2	g SO_2	% of Total	Sulfur Form
B-III-19	Steam Distillation 110°-120°C					
	5.5 liter water condensed in 19 hrs.	100.6	22.2	6.3	28.2	SO_2/H_2O
B-III-20	Aqueous Lime Slurry 100°C					
	40 g $Ca(OH)_2$ (=0.54 moles for 0.47 moles SO_2) and 150 ml water added to sample. Digested at 100°C for 2 hrs. Precipitate filtered, washed, dried. Weight: 47 g. Sulfur content: 12.6%, C 4.0%, H 0%. Distillation of filtrate to 150°C produced H_2S. Residue in still: 117.2 g, black, tar-like, malodorous.	134.7	29.8	11.8	39.6	$CaSO_3/CaS_2O_6$(2)
				1.0	3.4	H_2S
			Total	12.8	44.0	
B-III-21	Acid Treatment 100°-110°C					
	Addition of 50 ml H_2SO_4 1:1 and heating to 100°C produced a precipitate of elemental sulfur. Weight: 1.05 g. Distillation of filtrate to 150°C produced SO_2.	101.7	22.5	2.1	9.3	S
				11.8	52.5	SO_2/H_2O
			Total	13.9	61.8	

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(1) Sample A-III-27 contained 33.3 g SO_2 and 17.3 g H_2O per 100 g amine. It was prepared at 100°C with 100% SO_2.

(2) An iodometric titration showed 32% of the sulfur in the precipitate as sulfite.

of the triethanolamine-sulfur dioxide system with formation of hydrogen sulfide and organic thiocompounds, as well as sulfur dioxide. Black, malodorous tar-like residues were formed.

Table 14 shows, that in contrast to the room temperature system, complete recovery of the sulfur from a triethanolamine-sulfur dioxide system prepared at 100°C was not feasible by either steam distillation, liming, or acid distillation below the decomposition temperature of the system (135°C). The lime treatment produced hydrogen sulfide (as well as other malodorous thiocompounds) in addition to a precipitate containing probably dithionate, and other sulfur anions. The acid treatment produced a precipitate of elemental sulfur as well as gaseous sulfur dioxide.

We conclude that a method of stripping of sulfur values from the high temperature amine-sulfur dioxide system must be based on the chemistry of the sulfane disulfonates (thionates). Some of the principal possibilities include recovery as calcium or ammonium salts, either by direct precipitation or separation through resin or liquid ion exchange techniques. By adding acid, the sulfur could be recovered as a mixture of elemental sulfur, sulfur dioxide, sulfuric acid and free, stable sulfane disulfonic acid. This would require subsequent liming or electrolysis to regenerate the amine. Instead, the amine-sulfur dioxide system could be electrolyzed directly to give the above products. If markets were found for sulfane disulfonates, or their free acids, recovery of these products could be attractive. Otherwise oxidation to sulfate or reduction to sulfide would be required.

Air oxidation of all sulfur species to sulfate and precipitation as calcium sulfate might be a less desirable possibility, although the economics might be improved by using limestone rather than calcined lime in the isolation process. Economically more attractive might be the sulfate precipitation after the disproportionation of the sulfur species to the stable end products, sulfate and sulfide at elevated temperatures (liberation of 1/4 hydrogen sulfide and precipitation of 3/4 sulfate), according to the overall equation:

$$4SO_3^{2-} + 2H^+ \longrightarrow H_2S + 3SO_4^{2-}$$

Even more favorable would be a disproportionation to 1/3 elemental sulfur and 2/3 sulfate, according to:

$$3SO_3^{2-} \longrightarrow S + 2SO_4^{2-}$$

This reaction might require neutral or acid conditions (e.g. provided by carbon dioxide).

The direct reduction of all sulfur species to either hydrogen sulfide or elemental sulfur might be feasible under proper conditions. The reduction by tetraethylenepentamine at 170-200°C to yield hydrogen sulfide as reported earlier is one such example.

Finally, combining recovery schemes involving formation of hydrogen sulfide and sulfur dioxide might lead to a dual process, which would produce elemental sulfur via the Claus process.

3. Attempted Cycle Testing of Triethanolamine and Feasibility of Using Limestone in the Chemical Sulfur Desorption

An experiment was designed to test cycling of triethanolamine using sulfur dioxide absorption from a simulated flue gas and desorption by a lime slurry treatment. Although previous experiments had demonstrated that the lime desorption was incomplete and heating of the liquor produced decomposition, it appeared desirable to determine the loss of absorption capacity in cycling of this liquor.

The experiment was carried out by absorption of a simulated flue gas in triethanolamine as described in Section II of this report. As a consequence the absorbed sulfur was primarily present as sulfate. The results of the cycling experiment therefore were not representive of the expected actual conditions. In addition, an attempted mass balance was not meaningful because of unavoidable, significant losses in product during processing; the decrease of absorption capacity could, therefore, not be evaluated. The data obtained in the experiment are briefly summarized in Table 15.

In another experiment we evaluated the feasibility of replacing lime by limestone for the desorption of sulfate from an amine. This method might be of importance if stack gases would indeed produce sulfate in the amine or if one would oxidize the amine-sulfur dioxide system with air to produce sulfate. An aqueous solution of triethanolamine was neutralized with sulfuric acid to pH7 and refluxed with powdered limestone. The sample produced carbon dioxide gas, which was collected and identified by barium hydroxide solution. The aqueous solution had a pH of 9 at the conclusion of the experiment. The reaction:

$$[(HO\cdot CH_2\cdot CH_2)_3\,NH]_2\,SO_4 + CaCO_3 \longrightarrow CaSO_4 + N(CH_2\cdot CH_2\cdot OH)_3 + CO_2 + H_2O$$

appeared to proceed as indicated under these conditions. We therefore conclude that limestone stripping of sulfate might be a feasible procedure for amine regeneration.

Table 15

Cycling of Triethanolamine with Sulfur Dioxide Absorption from Simulated Flue Gas and Desorption by a Lime Slurry

Sample Code	Treatment	Analytical Results Nitrogen %	Sulfur %	SO_2 (g/100g TEA)	H_2O
A-III-30-7	SO_2/H_2SO_4 absorption from simulated flue gas (2000 l per 100g TEA)	7.04	10.12	27.0	6.5
B-III-30	Lime/H_2O	5.32	2.65	9.4	67.3
A-III-30-10	SO_2/H_2SO_4 absorption from simulated flue gas (~4000 l. per 100g TEA)	6.89	10.86	28.8	7.6

V. ENGINEERING COST ANALYSIS OF POTENTIAL HIGH TEMPERATURE AMINE ABSORPTION PROCESSES WITH CHEMICAL REGENERATION

The amine-based thermally regenerated sulfur dioxide absorption process concept (HiTRAAP) initially proposed for study in this program became unfeasible because of the unavoidable disproportionation of the sulfur dioxide in the amine into sulfur anions of higher and lower oxidation states. The further reactions between the sulfur species and the amine can be avoided by carrying out the absorption below a temperature characteristic for each amine (170°C for tetraethylenepentamine, 130°C for triethanolamine). In principle, therefore, chemical methods of regenerating the amine will be required. We speculated upon several potential methods which might be technically feasible and it was therefore necessary to gain some perspective on the comparative economics of some of these regeneration schemes as a guide for further work.

We carried out preliminary economic analyses for seven processes as shown in the Appendix to this report. An 800 megawatt single boiler central station was chosen as the model for the economic analysis. The general outline of the development of capital and operating costs parallels that of Sidney Katell of the U.S. Bureau of Mines.[6] It is of course recognized that many parameters are not illustrative of conventional utility practice and many other underlying assumptions in regard to the chemistry may be questionable. The economic data thus developed must be viewed cautiously. The primary value of the analysis is in the comparative evaluation of potential recovery schemes.

A summary of the engineering cost analysis is given in Table 16. It indicates that several amine-based absorption processes might be profitable and the costs for a number of amine-based processes compare favorably with those projected by Katell for the Alkalized Alumina, Catalytic Oxidation and Reinluft processes.

The engineering analysis for these processes involved simplifying assumptions regarding the process chemistry. Triethanolamine was used

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[6] Sidney Katell, Removing Sulfur Dioxide from Flue Gases, Chemical Engineering Progress 62 (No. 10), 67-73 (1966)

Table 16

AIR POLLUTION CONTROL PROCESS SUMMARY

Process	Investment $/kw	By-Product	By-Product Value (Debit)		Annual Pretax Cost (Credit) $/Yr.	Net Operating Cost (Credit)	
			$/Short Ton	$/Short Ton Sulfur		Mills/kwh	$/Ton Coal
Amine Based Systems							
Direct Reduction	6.45	Sulfur	40.00	40.00	(1,084,200)	(0.17)	(0.49)
Liquid Ion Exchange	9.00	$(NH_4)_2SO_4$	28.00	68.50	(467,300)	(0.07)	(0.21)
Resin Ion Exchange	16.35	$(NH_4)_2SO_4$	28.00	68.50	281,700	0.04	0.13
Lime	8.58	$CaSO_3$	10.70(1)	40.00	532,300	0.08	0.24
Limestone (2/3 of S)	8.64	Waste and Sulfur	(1.00) 40.00	10.00	1,321,800	0.21	0.60
Limestone	8.38	Waste	(1.00)	(10.00)	2,663,400	0.42	1.21
Lime	8.58	Waste	(1.00)	(10.00)	3,494,300	0.55	1.59
Electrolytic	17.82	100% H_2SO_4	15.00	49.00	3,751,500	0.57	1.64
Other Systems(2)							
Alkalized Alumina	10.64	Sulfur	40.00	140.00	1,000,000	0.16	0.45
Catalytic Oxidation	21.25	70% H_2SO_4	10.00	46.50	1,400,000	0.26	0.60
Reinluft	17.77	100% H_2SO_4	15.00	49.00	2,600,000	0.42	1.20

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(1) $CaSO_3$ valued as sulfur equivalent

(2) Ref: "Removing Sulfur Dioxide from Flue Gases", S. Katell, C.R.P., Vol. 62, No. 10, October 1966

as the model amine and the absorption system was kept at 212°F by evaporating water to avoid decomposition. As indicated earlier in the report, other amines could be used at higher temperatures, for example tetraethylenepentamine up to 340°F. Acid salts (mole ratio triethanolamine: sulfur dioxide = 1:1) were assumed throughout, instead of neutral salts, the formation of which was observed experimentally under the projected process conditions. The disproportionation of sulfite into dithionate and polythionates was disregarded and all reactions were treated as involving sulfite as the only sulfur anion. In reality, for example, the precipitation of calcium salts might be complicated by the presence of several sulfur species in place of sulfite. The recovered mixture of calcium salts, however, might have a higher by-product value than the sulfur-equivalent-value assumed for calcium sulfite. The liquid and resin ion exchange processes were credited with the by-product value of ammonium sulfate, assuming oxidation of all sulfur species to sulfate either before or after the ion exchange. The processes could also produce the pure ammonium salts of a variety of thionates as well as thiosulfate and the product credits for these salts might be different, assuming sufficient uses could be found or developed.

The credit achieved for the recovered sulfur is the major determinant of the cost of each process. Other factors are the investment required and the operating cost. This is born out when one compares the results of the engineering cost analysis as given in Table 16.

The most attractive process is a direct reduction of all sulfur species to elemental sulfur. The analysis assumes a reduction with hydrogen sulfide, which is purchased at a price of $38/ton; the sulfur is recovered from the amine. The process might be desirable in the vicinity of processing plants having hydrogen sulfide streams available. An alternate scheme for reduction to sulfur might be the reaction of the sulfur species with hydrogen, carbon monoxide, or hydrocarbons to produce hydrogen sulfide, which could then be converted to sulfur via the Claus process. At this time there is no indication for the technical feasibility of either scheme. The process scheme assuming reduction with hydrogen sulfide has very low investment and operating costs and the recovered sulfur value is high enough to give a net operating profit of $0.49/ton of coal.

The next two processes in decreasing profitability are based on ion exchange of the sulfur species and recovery as ammonium sulfate. The high credit of $68.50 per ton of recovered sulfur in the form of ammonium sulfate is primarily responsible for the better economics of these processes relative to others. The liquid ion exchange (solvent extraction) process is more attractive compared to the resin ion exchange scheme primarily because of lower investment costs. The processes might be good choices in areas with nearby fertilizer demands.

Next in increasing net operating cost is a process involving the precipitation of all sulfur species with lime and assuming a value for the resultant calcium salt equivalent to the contained sulfur (net operating cost $0.24/ton coal). If the product has no value and is charged with disposal costs of $1.00 per ton, the net operating costs for the process would increase to $1.59 per ton of coal. Between these two costs would be the net operating costs for processes involving the use of limestone in place of lime. The first is based on the recovery of one third of the sulfur as elemental sulfur and two thirds as gypsum-waste (assuming a disproportionation of the calcium salts of the sulfur species into these products) and the second assumes formation of a waste product only.

The last process involves the eletrolytic regeneration of the amine and production of sulfuric acid; the scheme is least economic because of high investment and operating costs and in spite of a high credit for the recovered sulfur.

In conclusion it appears that future efforts in the development of a viable process based on amines for the removal of sulfur dioxide from stack gases should be directed principally at a process scheme involving reduction of the sulfur species to elemental sulfur; this scheme has the lowest costs in the preliminary analysis. Ion exchange processes and recovery of ammonium sulfate should be considered as alternate schemes.

APPENDIX
ENGINEERING COST ANALYSIS

A. Process Descriptions

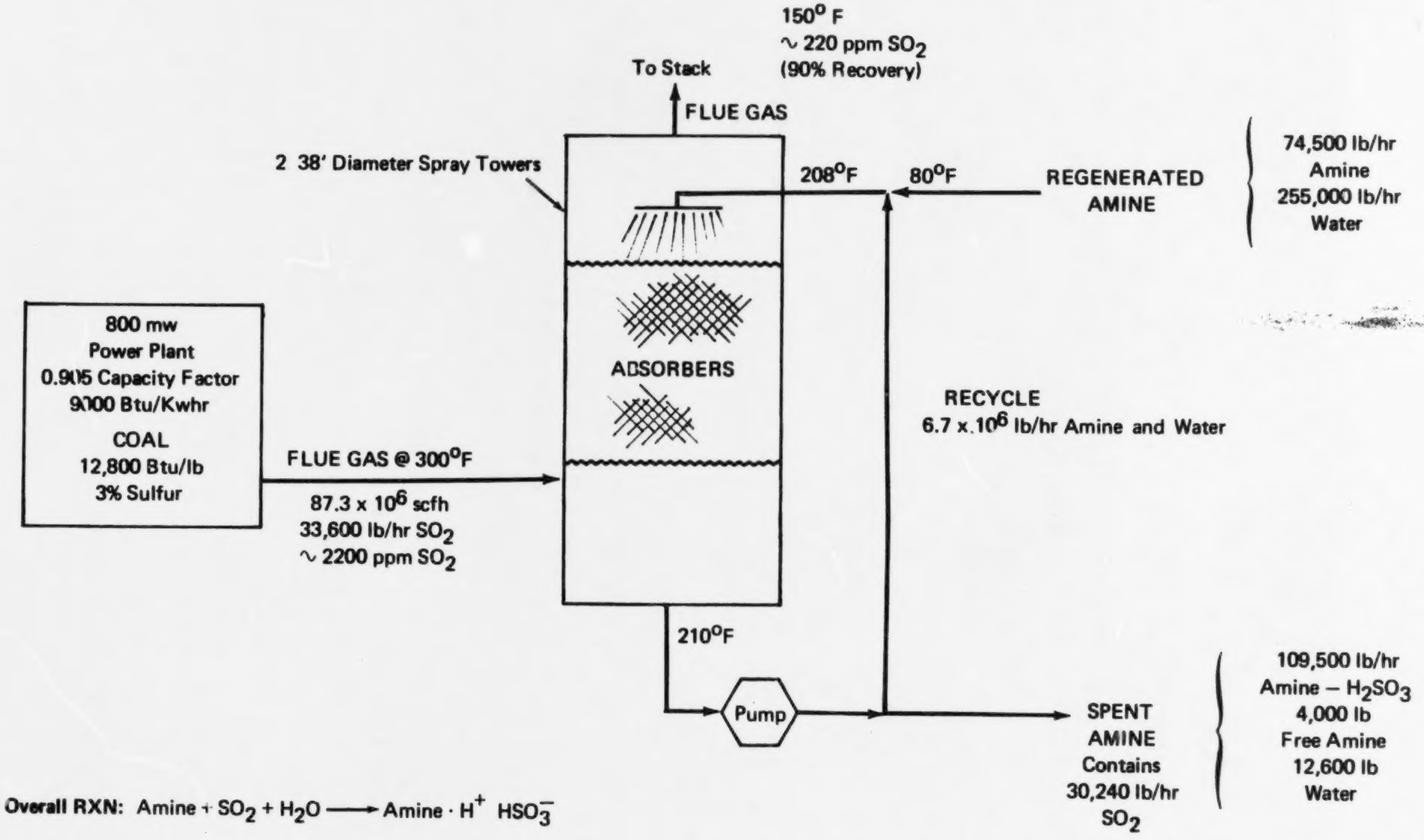
Absorption System: A spray-tower absorption system is used (Figure A1) with each regeneration process. Unreacted amine (triethanolamine) and recycled material would be dispersed in an up-flow tower at a gas-to-liquid flow rate ratio of unity. In passing through the absorber, the flue gas would evaporate sufficient water to keep the amine temperature below 200°F. The amine is drawn out at the bottom of the tower, a portion recycled, and the remainder pumped to the regeneration system.

The amount of water required to keep the temperature of the flue gas at or below 200°F is so high as to roughly double the water concentration in the leaving flue gas (to about 16%). The water concentration in the entering scrubbing liquor is about 22.8% and in the exit liquor about 19.3%. The scrubbing process is therefore not very different from an aqueous amine scrubbing process.

As indicated in Section V of this report the scrubbing process could also be designed to operate at the flue gas temperature between 200 and 350°F, if tetraethylenepentamine were chosen as absorbent in place of triethanolamine; this would eliminate the need for adding water to the system.

Regeneration Systems: In the following paragraphs the assumed chemical reactions and unit operations required for each of several regeneration systems are described. Although some of the reactions indicated are known to take place in certain temperature regimes and with certain amines, we must emphasize that the feasibility of these reactions was not evaluated with the amine sulfur dioxide products prepared in the course of this program.

1. Direct Reduction Regeneration - The direct reduction regeneration concept assumes that the amine bisulfite complex will undergo quantitative reaction with hydrogen sulfide gas in an aqueous medium precipitating


800 mw
Power Plant
0.905 Capacity Factor
9000 Btu/Kwhr
COAL
12,800 Btu/lb
3% Sulfur
FLUE GAS @ 300°F
87.3 x 10⁶ scfh
33,600 lb/hr SO2
∼ 2200 ppm SO2
2 38' Diameter Spray Towers
To Stack
FLUE GAS
150° F
∼ 220 ppm SO2
(90% Recovery)
208°F
80°F
REGENERATED AMINE
74,500 lb/hr
Amine
255,000 lb/hr
Water
ABSORBERS
RECYCLE
6.7 x 10⁶ lb/hr Amine and Water
210°F
Pump
SPENT AMINE
Contains
30,240 lb/hr
SO2
109,500 lb/hr
Amine – H2SO3
4,000 lb
Free Amine
12,600 lb
Water

Overall RXN: $\text{Amine} + SO_2 + H_2O \longrightarrow \text{Amine} \cdot H^+ \ HSO_3^-$

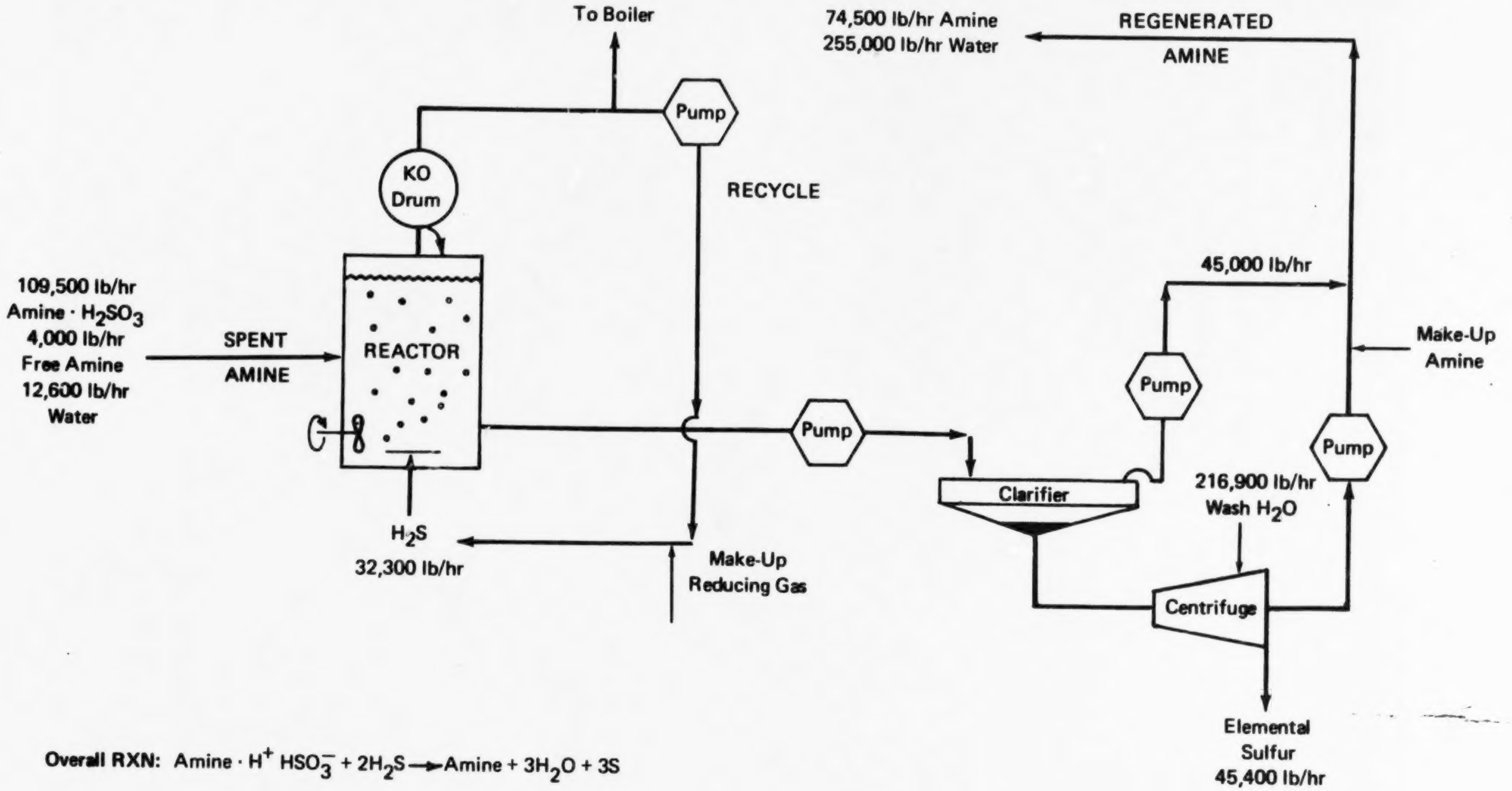
FIGURE A–1 ABSORPTION SECTION

elemental sulfur (Figure A2). The reactions involved are similar to the aqueous Claus reaction. In order to obtain favorable conversions, it may be necessary to maintain this solution in the acid pH range by stripping only a portion of the sulfur dioxide and recycling the remainder. The liquor from the reactor would be serviced to a clarifier, and the concentrated underflow centrifuged and washed. Elemental sulfur is discharged from the centrifuge and the amine is recycled. It is assumed that the hydrogen sulfide is available from other sources. Alternatively, the appropriate amount of sulfur could be reacted with water gas to provide the hydrogen sulfide.

2. Liquid Ion Exchange Regeneration - This process concept assumes that the amine-bisulfite adduct will react with an immiscible quaternary amine (QA) hydroxide to regenerate the amine and yield QA-bisulfite (Figure A3). The QA-bisulfite is then contacted with concentrated ammonium hydroxide to regenerate the QA and yield an ammonium sulfite solution. The ammonium sulfite solution is concentrated in an evaporator and crystallized. In drying the crystals, oxidation to ammonium sulfate probably will occur.

3. Resin Ion Exchange Regeneration - It is assumed that the bisulfite-amine salt is serviced to the ion exchange tower at a concentration near three weight percent (Figure A4). In the tower the bisulfite ion is exchanged for hydroxyl ion and the regenerated amine returned to the process. A highly basic resin would be required for this service. After one hour, the column saturates and the flow would be valved to another column.

The resin is regenerated with 4% ammonium hydroxide solution prepared from anhydrous ammonia and water. Ammonium sulfite would result. For some paper mill applications, the ammonium sulfite could be sent to process, but alternatively it could be concentrated using a quadruple effect evaporation system. The resulting crystal slurry would then be serviced to a rotary dryer where oxidation would probably occur to yield ammonium sulfate crystals.


To Boiler
74,500 lb/hr Amine
255,000 lb/hr Water
REGENERATED
AMINE
Pump
KO
Drum
RECYCLE
45,000 lb/hr
109,500 lb/hr
Amine · H2SO3
4,000 lb/hr
Free Amine
12,600 lb/hr
Water
SPENT
AMINE
REACTOR
Make-Up
Amine
Pump
Pump
Pump
Clarifier
216,900 lb/hr
Wash H2O
H2S
32,300 lb/hr
Make-Up
Reducing Gas
Centrifuge
Elemental
Sulfur
45,400 lb/hr

Overall RXN: $\text{Amine} \cdot \text{H}^+ \, \text{HSO}_3^- + 2\text{H}_2\text{S} \longrightarrow \text{Amine} + 3\text{H}_2\text{O} + 3\text{S}$

FIGURE A–2 DIRECT REDUCTION REGENERATION

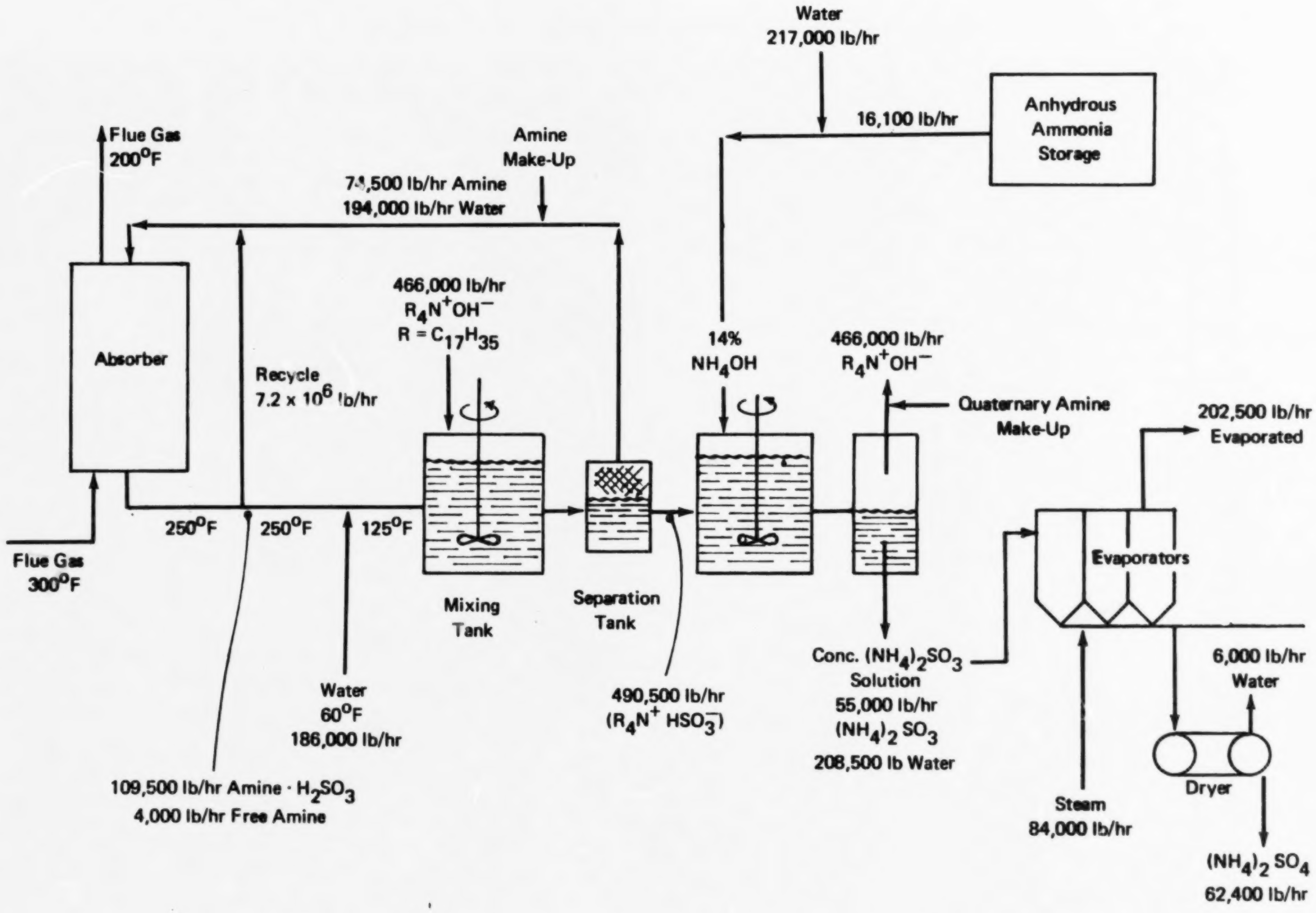
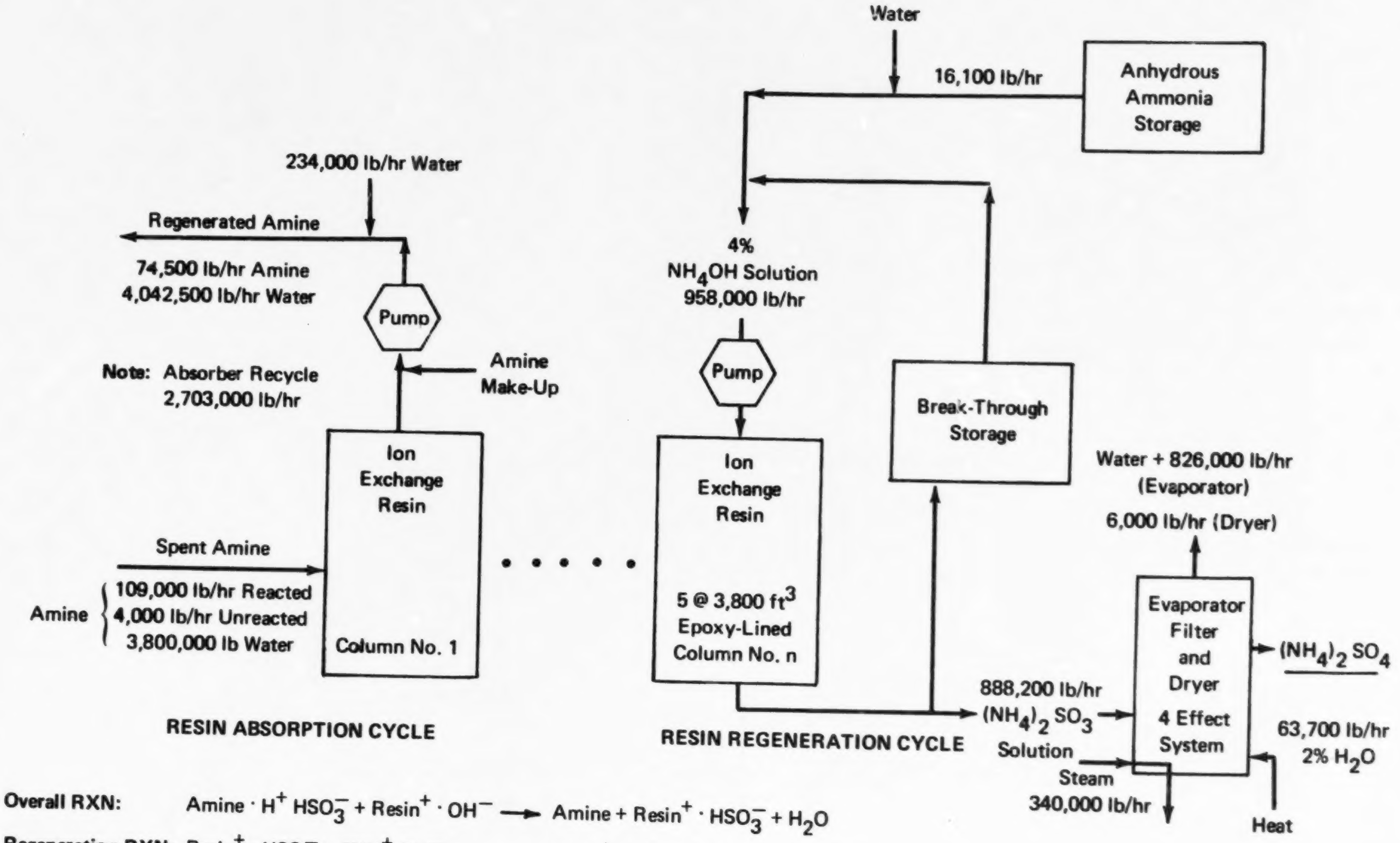

Water
217,000 lb/hr
16,100 lb/hr
Anhydrous Ammonia Storage
Flue Gas
200°F
Amine
Make-Up
74,500 lb/hr Amine
194,000 lb/hr Water
Absorber
Recycle
7.2 x 10⁶ lb/hr
466,000 lb/hr
R₄N⁺OH⁻
R = C₁₇H₃₅
14%
NH₄OH
466,000 lb/hr
R₄N⁺OH⁻
Quaternary Amine
Make-Up
202,500 lb/hr
Evaporated
Evaporators
250°F
250°F
125°F
Flue Gas
300°F
Mixing
Tank
Separation
Tank
Water
60°F
186,000 lb/hr
490,500 lb/hr
(R₄N⁺ HSO₃⁻)
Conc. (NH₄)₂SO₃
Solution
55,000 lb/hr
(NH₄)₂ SO₃
208,500 lb Water
6,000 lb/hr
Water
Dryer
Steam
84,000 lb/hr
109,500 lb/hr Amine · H₂SO₃
4,000 lb/hr Free Amine
(NH₄)₂ SO₄
62,400 lb/hr

FIGURE A–3 LIQUID ION EXCHANGE REGENERATION


Water
16,100 lb/hr
Anhydrous Ammonia Storage
234,000 lb/hr Water
Regenerated Amine
74,500 lb/hr Amine
4,042,500 lb/hr Water
Pump
Note: Absorber Recycle 2,703,000 lb/hr
Amine Make-Up
Ion Exchange Resin
Column No. 1
Spent Amine
Amine
109,000 lb/hr Reacted
4,000 lb/hr Unreacted
3,800,000 lb Water
4%
NH_4OH Solution
958,000 lb/hr
Pump
Ion Exchange Resin
5 @ 3,800 ft^3
Epoxy-Lined
Column No. n
Break-Through Storage
Water + 826,000 lb/hr (Evaporator)
6,000 lb/hr (Dryer)
Evaporator Filter and Dryer 4 Effect System
$(NH_4)_2SO_4$
888,200 lb/hr
$(NH_4)_2SO_3$ Solution
Steam
340,000 lb/hr
63,700 lb/hr
2% H_2O
Heat
RESIN ABSORPTION CYCLE
RESIN REGENERATION CYCLE

Overall RXN: $\text{Amine} \cdot H^+ HSO_3^- + \text{Resin}^+ \cdot OH^- \longrightarrow \text{Amine} + \text{Resin}^+ \cdot HSO_3^- + H_2O$

Regeneration RXN: $\text{Resin}^+ \cdot HSO_3^- + 2NH_4^+ OH^- \longrightarrow \text{Resin}^+ \cdot OH^- + (NH_4)_2SO_3 + H_2O$

Oxidation RXN: $2(NH_4)_2SO_3 + O_2 \text{ (Air)} \longrightarrow 2(NH_4)_2SO_4$

FIGURE A–4 RESIN ION EXCHANGE REGENERATION

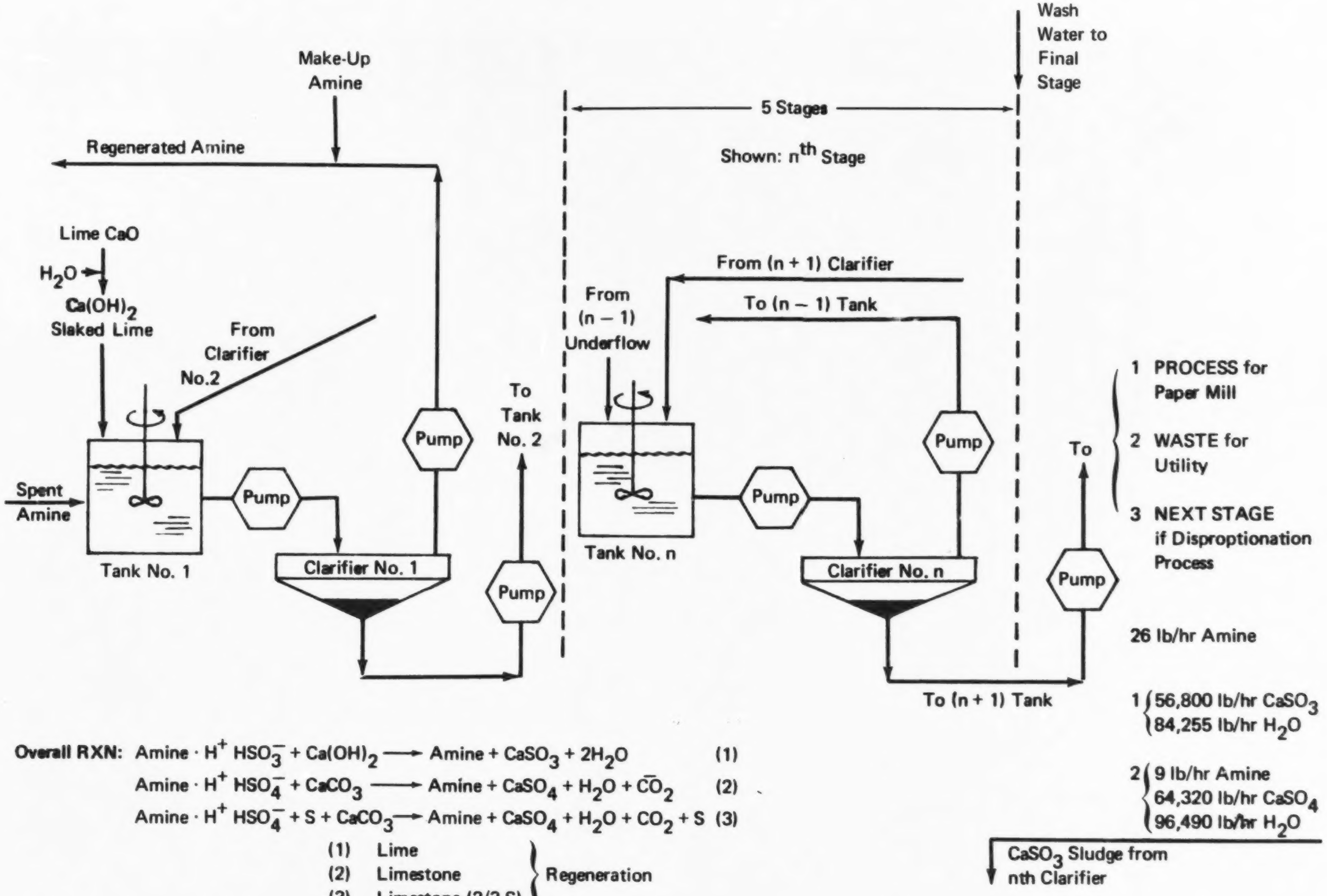
4. Lime Regeneration - Regeneration of the bisulfite-amine salt might be accomplished by agitation with slaked lime (Figure A5). Subsequent counter-current washing of the calcium sulfite slurry is required to recover the amine values entrained with the solid underflow from the clarifiers. A total of six stages of stirred tanks and clarifiers is required in order to reduce the value of the amine lost to a quantity less than the capital and operating cost of an additional stage.

It may be argued that the lime process is more costly and no more effective than where the flue gas is scrubbed directly with a lime slurry. The lime amine method has value, however, if an amine can be found such that absorption could take place in a non-aqueous system thus avoiding the need for reheat.

5. Limestone Regeneration - The use of limestone instead of lime for amine regeneration may be possible if the amine-bisulfite salt is oxidized to amine-bisulfate in the absorption tower. The process flowsheet (Figure A5) is similar to that for lime regeneration.

6. Limestone Regeneration of Disproportionated Sulfite - A reaction has been postulated wherein three sulfite ions disproportionate to yield two sulfate ions and elemental sulfur. If this reaction occurs, the sulfate ion could be precipitated with limestone, thus regenerating the amine (Figures A5 and A6). The sulfur could be extracted from the calcium sulfate slurry using an immiscible solvent such as xylene. The xylene might be evaporated yielding molten sulfur. The xylene would then be condensed and recycled to the extraction vessel.

7. Electrolytic Reduction - The electrolytic reduction process assumes that the amine bisulfite salt can be electrolytically split to yield regenerated amine, hydrogen, sulfur dioxide, and oxygen. (Figure A7) Oxygen is released with the sulfur dioxide so that the mixture, with added air, could be sent directly to a sulfuric acid plant. The sulfuric acid plant would not require sulfur burners or high temperature filters and thus should be more economical than a conventional plant.


Make-Up Amine
Regenerated Amine
Lime CaO
H_2O
$Ca(OH)_2$ Slaked Lime
From Clarifier No.2
Spent Amine
Tank No. 1
Pump
Clarifier No. 1
Pump
Pump
To Tank No. 2
5 Stages
Shown: n^{th} Stage
Wash Water to Final Stage
From (n – 1) Underflow
From (n + 1) Clarifier
To (n – 1) Tank
Tank No. n
Pump
Pump
Clarifier No. n
To (n + 1) Tank
Pump
To
1 PROCESS for Paper Mill
2 WASTE for Utility
3 NEXT STAGE if Disproportionation Process
26 lb/hr Amine
1 56,800 lb/hr $CaSO_3$
84,255 lb/hr H_2O
2 9 lb/hr Amine
64,320 lb/hr $CaSO_4$
96,490 lb/hr H_2O
$CaSO_3$ Sludge from nth Clarifier

Overall RXN:

$$\text{Amine} \cdot H^+ HSO_3^- + Ca(OH)_2 \longrightarrow \text{Amine} + CaSO_3 + 2H_2O \qquad (1)$$

$$\text{Amine} \cdot H^+ HSO_4^- + CaCO_3 \longrightarrow \text{Amine} + CaSO_4 + H_2O + CO_2 \qquad (2)$$

$$\text{Amine} \cdot H^+ HSO_4^- + S + CaCO_3 \longrightarrow \text{Amine} + CaSO_4 + H_2O + CO_2 + S \qquad (3)$$

$$\left.\begin{array}{ll} (1) & \text{Lime} \\ (2) & \text{Limestone} \\ (3) & \text{Limestone (2/3 S)} \end{array}\right\} \text{Regeneration}$$

FIGURE A–5 LIME (LIMESTONE) REGENERATION

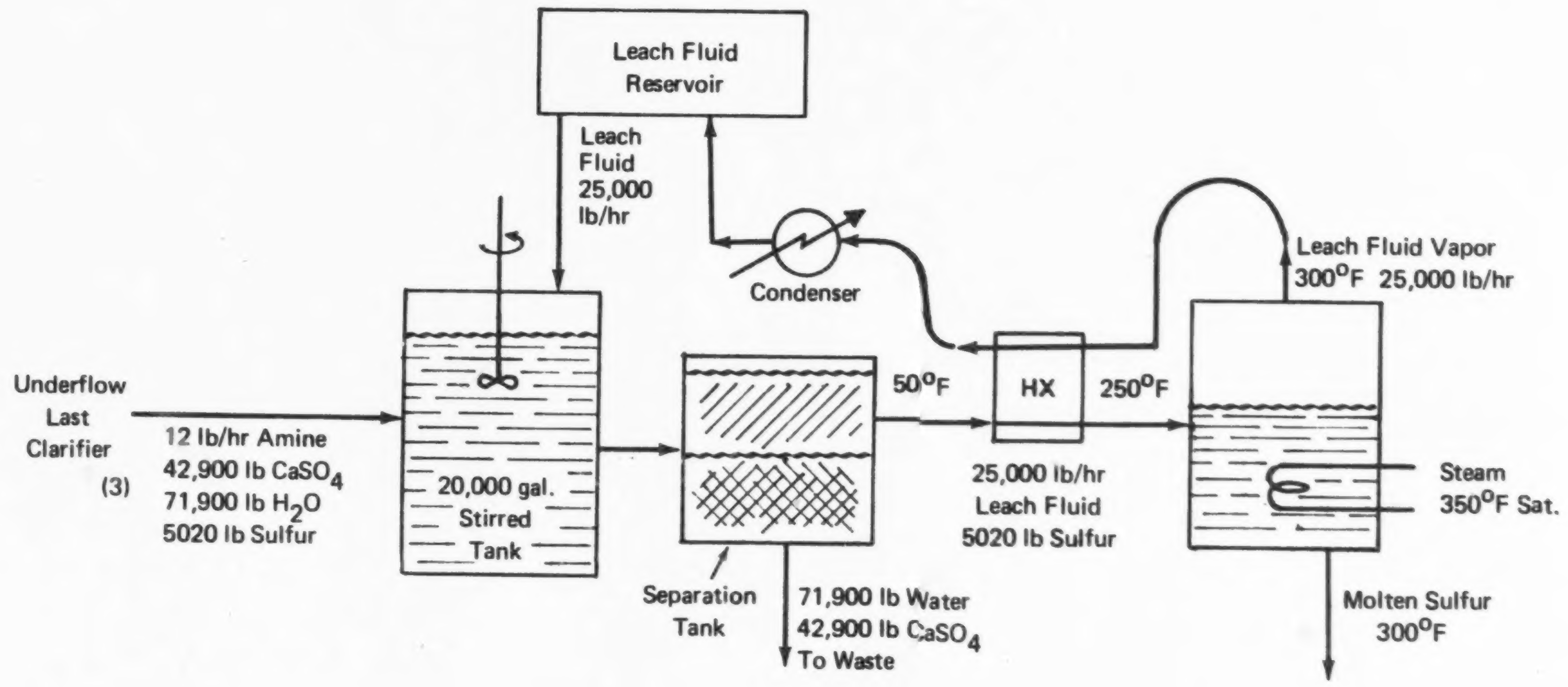
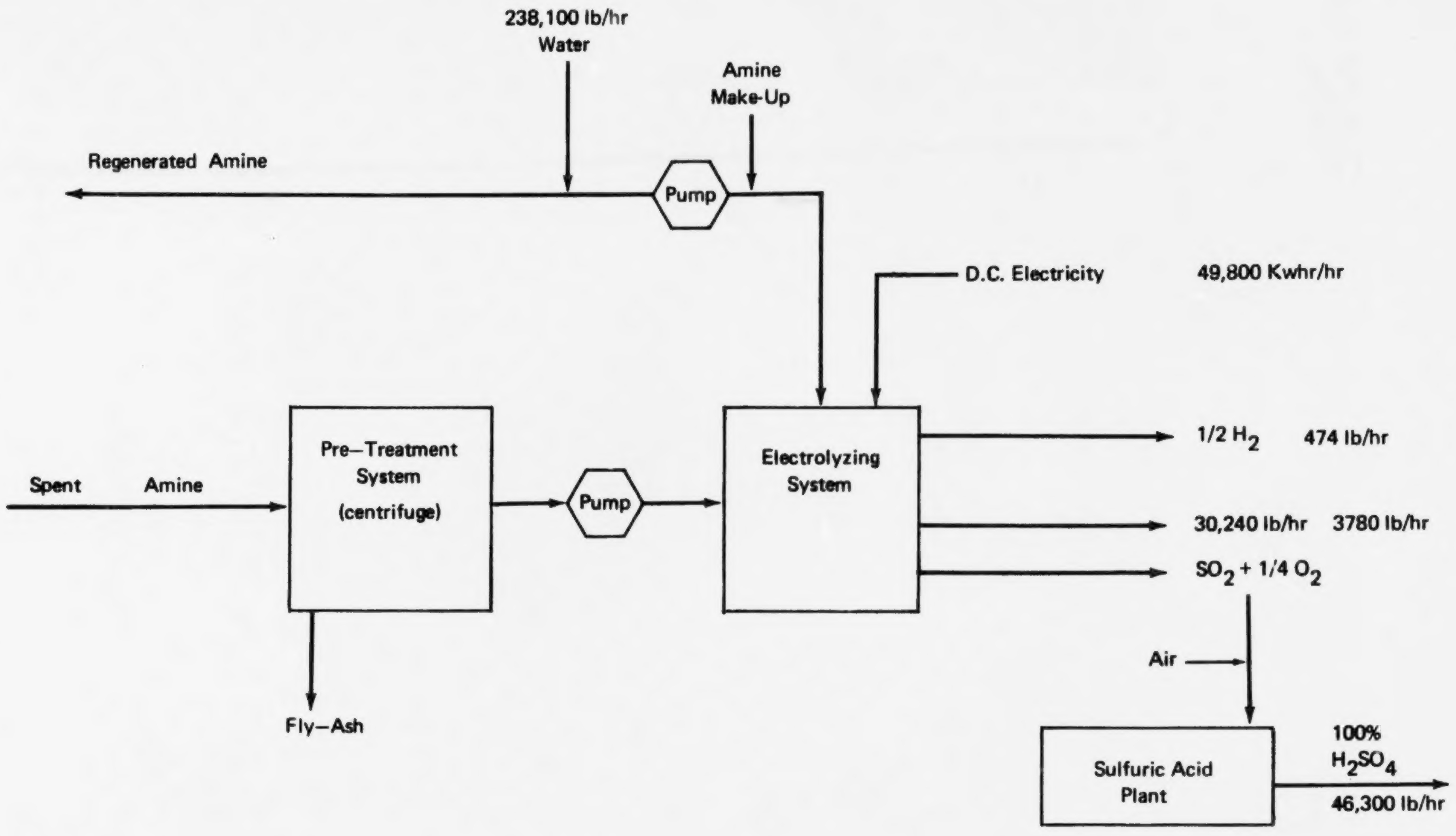

Leach Fluid Reservoir
Leach Fluid 25,000 lb/hr
Condenser
Leach Fluid Vapor 300°F 25,000 lb/hr
Underflow Last Clarifier (3)
12 lb/hr Amine
42,900 lb $CaSO_4$
71,900 lb H_2O
5020 lb Sulfur
20,000 gal. Stirred Tank
50°F
HX
250°F
25,000 lb/hr Leach Fluid 5020 lb Sulfur
Steam 350°F Sat.
Separation Tank
71,900 lb Water
42,900 lb $CaSO_4$
To Waste
Molten Sulfur 300°F

FIGURE A–6 LIMESTONE REGENERATION OF DISPROPORTIONATED SULFITE


238,100 lb/hr
Water
Amine
Make-Up
Regenerated Amine
Pump
D.C. Electricity
49,800 Kwhr/hr
Spent Amine
Pre–Treatment
System
(centrifuge)
Pump
Electrolyzing
System
1/2 H2 474 lb/hr
30,240 lb/hr 3780 lb/hr
SO2 + 1/4 O2
Fly–Ash
Air
Sulfuric Acid
Plant
100%
H2SO4
46,300 lb/hr

Overall RXN: $2\ \text{Amine} \cdot H^+\ HSO_3^- \longrightarrow 2\ \text{Amine} + \overline{H}_2 + 2\ \overline{SO}_2 + 1/2\ \overline{O}_2 + H_2O$

FIGURE A–7 ELECTROLYTIC REGENERATION

B. Assumptions Used in Economic Evaluation

The following assumptions have been made in the calculations:

a. General

1. Coal Analysis:

	%
Carbon	70.1
Oxygen	6.6
Hydrogen	4.9
Nitrogen	1.4
Sulfur	3.0
Ash	12.7
Moisture	1.3
TOTAL	100.0

2. Coal Combustion:

• Excess air	20 percent
• Coal burned	280 tons/hr
• Heating value	12,800 Btu/lb

3. Flue Gas from 800 Megawatt Power Plant: 87.3 Million standard cubic feet/hr

4. Sulfur in Coal: 100% Burns to SO_2

5. Capital Items Estimation:

- Yearly maintenance (labor, supervision, material); 3% Of depreciation base
- Installation costs taken at 2 times bare equipment costs
- Plant facilities: 5% Of cost of unit

- Plant utilities: 7% Of cost of unit plus plant facilities

6. Investment: 14% Annually (includes depreciation, taxes, insurance, and return on investment)

7. Absorber Section:

   - Triethanolamine (MW=149) was assumed as the absorbent
   - Two spray tower absorbers would be used
   - A gas flow rate of approximately 11 feet per second was assumed for the towers
   - It was assumed that the flue gas entered at 300°F and left the absorber having experienced 90% SO_2 removal
   - Amine losses average 4% of the hourly flow to the absorber section per day

b. Direct Reduction Regeneration

1. Residence time of liquid stream in reactor was one minute
2. Centrifuge: 36" Diameter by 96" long with 200 connected HP
3. Clarifier settling rate: 25 Sq ft per ton per 24 hours
4. Hydrogen sulfide charged at a rate equivalent to the sulfur value for a sulfur price of $40 per short ton

c. Liquid Ion Exchange

1. $(C_{17}H_{34})_4N^+OH^-$ was assumed as the quaternary ammonium compound for liquid exchange
2. To avoid degradation of the quaternary amine, the dry absorber effluent was cooled to 125°F by the addition of water

3. Regenerant ammonium hydroxide was fed at 14% concentration and the ammonium sulfite services to quadruple effect, backward-feed evaporators
4. Average residence time in contacting reactors and separation tanks was six minutes
5. Two, 60 Mlb/hr gas- or oil-fired package boilers were required to service the evaporators

d. Resin Ion Exchange

1. Absorber was operated with an inlet absorbent concentration of 3%
2. Resin capacity was assumed at 0.8 gram milliequivalents per milliliter of wet resin. Resin cost was taken at $50 per cubic foot (wet). 5% Resin loss per year
3. Regenerent ammonium hydroxide was fed at 5% concentration and the ammonium sulfite serviced to quadruple effect, backward feed evaporators
4. Towers were sized to saturate in one hour
5. Two, 175 Mlb/hr gas- or oil-fired package boilers were required to service the evaporators

e. Lime or Limestone Regeneration Processes

1. Underflow of clarifiers assumed at 40% solids
2. Mean residence time in tankage was approximately two minutes
3. Clarifier settling rate: 25 tons/square foot per day

f. Electrolytic Regeneration

1. Current efficiency was assumed to be 95%
2. Current density was assumed to be 93 amperes per square foot
3. Electrical Consumption was assumed to be 105 kilowatt hours per pound mole electrolyzed

C. Engineering Cost Estimates

Plant investment and operating costs are summarized in the following tables for the various absorption-regeneration processes. All estimations are based on installation with an 800 megawatt coal-fired boiler and do not necessarily represent the most economical configuration. It is assumed that the processes are added on to an existing power plant and no charges are made for acquisition of real estate. Some savings in duct work or equipment no longer required would be realized using these processes with new facilities.

The plant utilities and facilities have been included at a fixed percentage of capital and are assumed to include steam and power distribution, instrument air, sanitary facilities, fire protection, administrative buildings, shops, etc.

For processes dealing with amine at low pH, epoxy linings or stainless steel construction was assumed for corrosion resistance.

Table A-1

DIRECT REDUCTION WITH H_2S

I. Working Capital

Amine supply (60 days) 216,000 lb @ $0.15/lb	$ 32,400
Direct labor, 3 months (direct + maintenance)	31,800
18.5% Payroll overhead, 3 months	5,900
Operating supplies, 3 months	7,200
Indirect costs, 4 months	37,600
Fixed cost, 0.5% of insurance base	24,300
Spare parts	48,000
Total	$ 187,200

II. Capital Requirements

Absorption section	$3,380,200
Regeneration section	909,000
Plant facilities	214,500
Plant utilities	300,200
Total construction	$4,803,900
Initial amine (330,000 lb @ $0.15/lb)	49,500
Total plant cost (insurance and tax bases)	$4,853,400
Interest during construction @ 2-1/2%	120,100
Working captital	187,200
Total investment	$5,160,700

DIRECT REDUCTION WITH H_2S (Continued)

III. Operating Cost

Direct cost:		
Raw materials and utilities:		
Power, 420 kw X 7920 hr X $0.006/kwhr	$ 20,000	
Water, 206,000 M gal/yr X $0.10/M gal	20,600	
H_2S, 16.1 ton/hr X 7920 hr/yr X $38/ton	4,840,000	
Amine, 982,000 lb/yr @ $0.15/lb	147,000	
		$5,027,600
Direct labor:		
48 man-hr/day, $2.75/man-hr. X 365 days	$ 48,000	
Supervision, 15% of labor	7,200	
		$ 55,200
Plant maintenance:		
10 Men, $6,000/yr	$ 60,000	
Supervision, 20%	12,000	
Material	72,100	
		$ 144,100
Payroll overhead, 18.5% of payroll		23,600
Operating supplies, 20% of maintenance		28,800
Total direct cost		$5,279,300
Indirect cost (administration and general overhead), 50% labor, maintenance, and supplies		114,000
Total capital charges, 14% of total investment		722,500
Gross operating cost		$6,115,800
Credit for 180M tons/yr of sulfur, $40/ton	$7,200,000	
Net operating pretax revenue		$1,084,200

Table A-2

LIQUID ION EXCHANGE

I. Working Capital

Amine supply (60 days) 216,000 lb @ $0.15/lb	$ 32,400
Direct labor, 3 months (direct + maintenance)	40,800
18.5% Payroll overhead, 3 months	7,500
Operating supplies, 3 months	8,800
Indirect costs, 4 months	44,200
Fixed costs, 0.5% of insurance base	25,200
Spare parts	59,100
NH_3 Supply (60 days)	522,000
Quaternary amine supply (60 days) 112 M lb @ $0.25/lb	279,400
Total	$1,036,700

II. Capital Requirements

Absorption section	$3,380,200
Liquid exchange section	1,876,800
Plant facilities	262,800
Plant utilities	386,400
Total construction	$5,906,200
Initial amine (330,000 lb @ $0.15/lb)	49,500
Initial quaternary amine (310,000 lb @ $0.25/lb)	77,400
Total plant cost (insurance and tax base)	$6,033,100
Interest during construction @ 2 1/2%	147,700
Working capital	1,036,700
Total investment	$7,217,500

LIQUID ION EXCHANGE (Continued)

III. Operating Cost

Direct Cost:		
Raw materials and utilities:		
Amine 982,000 lb/yr @ $0.15/lb	$ 147,000	
Quaternary Salt 6140 M lb/yr @ $0.25/lb	1,535,000	
Ammonia 8.05 tons/hr X 7920 hrs X $45/ton	2,870,000	
Water, 380,000 M gal/yr X $0.10/M gal	38,000	
Power, 1260 kw X 7920 hrs X $0.006/kw	60,000	
Steam, 90 M lb/hr X 7920 hrs X $0.50/M lb	356,400	
		$5,006,400
Direct labor:		
48 man hr/day, $2.75/man hr X 365 days	48,000	
Supervision, 15% of labor	7,200	
		$ 55,200
Plant maintenance:		
15 Men @ $6,000/yr	$90,000	
Supervision, 20%	18,000	
Material	69,200	
		$177,200
Payroll overhead, 18.5% of payroll		30,200
Operating supplies, 20% of maintenance		35,400
Total direct cost		$5,304,400
Indirect cost (administration and general overhead), 50% labor maintenance and supplies		133,900
Total capital charges, 14% of total investment		1,010,400
Gross operating cost		$6,448,700
Credit for sale of 247 M tons/yr $(NH_4)_2SO_4$ at $28/ton	$6,916,000	
Net operating pretax revenue		$ 467,300

Table A-3

RESIN ION EXCHANGE

I. Working Capital

Amine supply (60 days) 216,000 lb @ \$0.15/lb	\$ 32,400
Direct labor, 3 months (direct + maintenance)	82,200
18.5% Payroll overhead, 3 months	15,200
Operating supplies, 3 months	16,300
Indirect costs, 4 months	84,100
Fixed cost, 0.5% of insurance base	59,400
Spare parts	108,900
NH_3 Supply (60 days)	522,000
Resin supply (60 days) 172 ft^3 @ \$50/ft^3	8,600
Total	\$829,100

II. Capital Requirements

Absorption section	\$3,314,000
Ion exchange equipment	3,330,000
Product treatment equipment	3,045,000
Plant facilities	484,400
Plant utilities	712,100
Total construction	\$10,885,500
Initial amine (330,000 lb @ \$0.15/lb)	49,500
Initial resin (18,900 ft^3 @ \$50/ft^3)	945,000
Total plant cost (insurance and tax bases)	\$11,880,000
Interest during construction @ 2-1/2%	272,100
Working capital	929,100
Total investment	\$13,081,200

RESIN ION EXCHANGE (Continued)

III. Operating Cost

Direct cost:		
Raw materials and utilities:		
Steam, 370 M lb/hr X 7920 hr X $0.50/M lb	$1,460,000	
Power, 1300, kw X 7920 hr X $0.007/kwhr	61,800	
Water, 129.7 M gal/hr X 7920 hr/yr X $0.10/ M gal	102,500	
NH_3 (anh), 63,800 tons/yr @ $45/ton	2,870,000	
R[illegible] make-up 945 ft^3/yr @ $50/$ft^3$	47,300	
[illegible]e, 982,000 lb/yr @ $0.15/lb	147,000	
		$4,688,600
Direct labor:		
96 Man-hr/day, $2.75/man-hr. X 365 days	$ 98,000	
Supervision, 15% of labor	14,700	
		$ 112,700
Plant maintenance:		
30 Men, $6,000/yr	$ 180,000	
Supervision, 20%	36,000	
Material	110,600	
		$ 326,600
Payroll overhead, 18.5% of payroll		60,800
Operating supplies, 20% of maintenance		65,300
Total direct cost		$5,254,000
Indirect cost (administration and general overhead), 50% labor, maintenance, and supplies		252,300
Total capital charges, 14% of investment		1,831,400
Gross operating cost		$7,337,700
Credit for 252 M tons/yr of $(NH_3)_2 SO_4$, $28/ton	$7,056,000	
Net operating pretax revenue		$ (281,700)

Table A-4

LIME REGENERATION

I. Working Capital

Amine supply (60 days) 216,000 lb @ $0.15/lb	$32,400
Direct labor, 3 months (direct + maintenance)	40,800
18.5% Payroll overhead, 3 months	7,500
Operating supplies, 3 months	9,300
Indirect costs, 4 months	45,900
Fixed cost, 0.5% of insurance base	31,200
Spare parts	62,000
Lime supply (60 days), 19,100 tons X $12/ton	229,000
Total	$458,100

II. Capital Requirements

Absorption section	$3,380,200
Regeneration section	2,140,000
Plant facilities	276,000
Plant utilities	405,700
Total construction	6,201,900
Initial amine (330,000 lb @ $0.15/lb)	49,500
Total plant cost (insurance and tax bases)	$6,251,400
Interest during construction @ 2 1/2%	155,000
Working capital	458,100
Total investment	$6,864,500

LIME REGENERATION (Continued)

III. Operating Cost

Direct cost:		
Raw materials and utilities:		
Power, 1093 kw X 7920 hrs X $0.006/kwhr	$ 52,000	
Water, 3.03 X 10^5 M gal X $0.10/M gal	30,300	
Amine make-up (overall), 1,188,000 lb/yr @ $0.15/lb	178,000	
Lime, 105,000 tons/yr X $12/ton	1,263,000	
		$1,523,300
Direct labor:		
48 man-hr/day, $2.75/man-hr. X 365 days	$ 48,000	
Supervision, 15% of labor	7,200	
		$ 55,200
Plant maintenance:		
15 men, $6,000/yr	$ 90,000	
Supervision, 20%	18,000	
Material	78,100	
		$ 186,100
Payroll overhead, 18.5% of payroll		30,200
Operating supplies, 20% of maintenance		37,200
Total direct cost		$1,832,300
Indirect cost (administration and general overhead), 50% labor, maintenance, and supplies		139,200
Total capital charges, 14% of total investment		961,100
Gross operating cost		$2,932,300
A. If $CaSO_3$ is without value		
Debit for disposal of 562 M tons/yr of $CaSO_3$ (40%), $1/ton	$ 562,000	
Net operating pretax revenue		$(3,494,300)
B. If $CaSO_3$ has value		$ 2,932,300
Credit for recovery of 225 M tons/yr of $CaSO_3$, $10.70/ton	$2,400,000	
Net operating pretax revenue		$ (532,300)

Table A-5

LIMESTONE REGENERATION

I. Working Capital

Amine supply (60 days) 216,000 lb @ $0.15/lb	$ 32,400
Direct labor, 3 months (direct + maintenance)	40,800
18.5% Payroll overhead, 3 months	7,500
Operating supplies, 3 months	9,300
Indirect costs, 4 months	45,900
Fixed cost, 0.5% of insurance base	31,200
Spare parts	62,000
Lime supply (60 days), 19,100 tons X $12/ton	68,200
Total	$297,300

II. Capital Requirements

Absorption section	$3,380,200
Regeneration section	2,140,000
Plant facilities	276,000
Plant utilities	405,700
Total construction	$6,201,900
Initial amine (330,000 lb @ $0.15/lb)	49,500
Total plant cost (insurance and tax bases)	$6,251,400
Interest during construction @ 2 1/2%	155,000
Working capital	297,300
Total investment	$6,703,700

LIMESTONE REGENERATION (Continued)

III. Operating Cost

Direct cost:		
Raw materials and utilities:		
Power, 1093 kw X 7920 hrs X $0.006/kwhr	$ 52,000	
Water, 3.1 X 10^5 M gal X $0.01/M gal	31,000	
Amine make-up (overall), 1,188,000 lb/yr @ $0.15/lb	178,000	
Limestone, 188,000 tons/yr X $2/ton	376,000	
		$ 637,000
Direct labor:		
48 Man-hr/day, $2.75/man-hr. X 365 days	$ 48,000	
Supervision, 15% of labor	7,200	
		$ 55,200
Plant maintenance:		
15 Men, $6,000/yr	$ 90,000	
Supervision, 20%	18,000	
Material	78,100	
		$ 186,100
Payroll overhead, 18.5% of payroll		30,200
Operating supplies, 20% of maintenance		37,200
Total direct cost		$ 945,700
Indirect cost (administration and general overhead), 50% labor, maintenance, and supplies		139,200
Total capital charges, 14% of total investment		938,500
Gross operating cost		$2,023,400
Debit for disposal of 640,000 tons/yr of $CaSO_4$ (40%), $1/ton	$640,000	
Net operating pretax revenue		$(2,663,400)

Table A-6

LIMESTONE TREATMENT OF DISPROPORTIONATED SULFITE

I. Working Capital

Amine supply (60 days) 216,000 lb @ $0.15/lb	$ 32,400
Direct labor, 3 months (direct + maintenance)	46,200
18.5% Payroll overhead, 3 months	8,500
Operating supplies, 3 months	9,600
Indirect cost, 4 months	47,600
Fixed cost, 0.5% of insurance base	32,300
Spare parts	64,200
Limestone supply (60 days), 22,600 tons X $2/ton	45,200
Leaching fluid supply (60 days), 1750 lb @ $0.04/lb	100
Total	$286,100

II. Capital Requirements

Absorption section	$3,380,200
Regeneration section	2,140,000
Sulfur recovery section	208,500
Plant facilities	286,400
Plant utilities	410,000
Total construction	$6,416,100
Initial leaching fluid (25,000 lb @ $0.04/lb)	1,000
Initial amine (330,000 lb @ $0.15/lb)	49,500
Total plant cost (insurance and tax bases)	$6,466,600
Interest during construction @ 2 1/2%	160,400
Working capital	286,100
Total investment	$6,913,100

LIMESTONE TREATMENT OF DISPROPORTIONATED SULFITE (Continued)

III. Operating Cost

Direct cost:		
Raw materials and utilities:		
Power, 1150 kw X 7920 hrs X $0.006/kwhr	$ 54,600	
Water, 2.9 X 10^5 M gal/yr X $0.10/M gal	29,000	
Amine make-up (overall), 1,188,000 lb/yr @ $0.15/lb	178,000	
Limestone, 125,000 tons/yr X $2/ton	250,000	
Leaching fluid, 100,000 lb/yr X $0.04/lb	4,000	
		$ 515,600
Direct labor:		
48 Man-hr/day, $2.75/man-hr X 365 days	48,000	
Supervision, 15% of labor	7,200	
		$ 55,200
Plant maintenance:		
18 Men, $6,000/yr	$ 108,000	
Supervision, 20%	21,600	
Material	62,900	
		$ 192,500
Payroll overhead, 18.5% of payroll		34,200
Operating supplies, 20% of maintenance		38,500
Total direct cost		$ 836,000
Indirect cost (administration and general overhead), 50% labor, maintenance, and supplies		143,100
Total capital charges, 14% of investment		967.800
Gross operating cost		$1,946,900
Credit for 19.8 M tons/yr of sulfur, $40/ton	$ 795,000	
Debit for disposal of 169.9 M tons/yr of $CaSO_4$, $1/ton	169,900	
Net operating pretax revenue		$(1,321,800)

Table A-7

ELECTROLYTIC REGENERATION

I. Working Capital

Amine supply (60 days) 216,000 lb @ $0.15/lb	$ 32,400
Direct labor, 3 months (direct + maintenance)	74,800
18.5% Payroll overhead, 3 months	13,800
Operating supplies, 3 months	20,100
Indirect costs, 4 months	94,400
Fixed cost, 0.5% of insurance base	67,200
Spare parts	134,400
Total	$437,100

II. Capital Requirements

Absorption section	$ 3,380,200
Electrolyzing section	7,000,000
Sulfuric acid plant	1,580,000
Plant facilities	598,000
Plant utilities	879,000
Total construction	$13,437,200
Initial amine (333,000 lb @ $0.15 lb)	49,500
Total plant cost (insurance and tax bases)	$13,486,700
Interest during construction @ 2 1/2%	335,900
Working capital	437,100
Total investment	$14,259,700

ELECTROLYTIC REGENERATION (Continued)

III. Operating Cost

Direct cost:		
Raw materials and utilities:		
Amine, 982,000 lb/yr @ $0.15/lb	$ 147,000	
Power, 50,960 kwhr/hr X 7920 hr X $0.006/kw	2,420,000	
Water, 2.26 X 10^5 M gal/yr X $0.10/M gal	22,600	
Catalyst (H_2SO_4 plant)	20,000	
Cell parts (5-year life)	1,000,000	
		$3,609,600
Direct labor:		
72 Man-hr/day, $2.75/man-hr X 365 days	$ 72,300	
Supervision, 15% of labor	10,800	
		$ 83,100
Plant maintenance:		
30 Men, $6,000/yr	$ 180,000	
Supervision, 20%	36,000	
Material	187,100	
		$ 403,100
Payroll overhead, 18.5% of payroll		55,400
Operating supplies, 20% of maintenance		80,600
Total direct cost		$4,231,800
Indirect cost (administration and general overhead), 50% labor, maintenance, and supplies		283,400
Total capital charges, 14% of investment		1,996,300
Gross operating cost		$6,511,500
Credit for 184 M tons/yr of 100% H_2SO_4, $15/ton	$2,760,000	
Net operating pretax revenue		$(3,751,500)

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